SURFACE WATER MONITORING FOR PESTICIDES IN THE HUPA AND KARUK TERRITORIES

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STATE OF CALIFORNIA
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Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
Environmental Hazards Assessment Program
830 K Street
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ABSTRACT

This study addressed the concerns expressed by Native Americans in the northwestern California on the use of pesticides (herbicides and insecticides) that may runoff into surface waters. These surface waters are important as drinking sources or as habitats for fish and wildlife. The study areas covered the Hupa and Karuk tribal and ancestral territories within Humboldt, Siskiyou, and Trinity counties.

The Environmental Hazards Assessment Program of the Department of Pesticide Regulation (DPR) monitored six sites on creeks and rivers. These sites included the Trinity River at Tish Tang campground, Supply Creek, Pine Creek, Klamath River at Horse Creek Bridge, Scott River at Hwy 96, and Elk Creek. Sampling was timed for the highest likelihood of detecting pesticide residues by taking sample following a rainstorm after substantial pesticide applications have been made. Sampling was conducted on four occasions from September 1998 to October 1999. Samples collected at the creek sites were analyzed for the following 13 herbicides: 2,4-D, atrazine, bromacil, cyanazine, diuron, glyphosate, hexazinone, MCPA, metribuzin, prometon, prometryn, simazine, and triclopyr. The samples collected from the river sites were analyzed for the 13 herbicides and 19 insecticides. The insecticides belong to two chemical classes, the organophosphates and the carbamates: 1) the organophosphates: azinphos-methyl, chlorpyrifos, DDVP, diazinon, dimethoate, ethoprop, fonofos, malathion, methidathion, methyl parathion, phosalone, phosmet, phorate; and 2) the carbamates: aldicarb, carbaryl, carbofuran, methiocarb, methomyl, and oxamyl.

Pesticide use reports and rainfall data were collected and reviewed to provide interpretation of results. A total of 40,631 pounds of active ingredient were applied within the effective watersheds of the sampling area during the study period. During this time, the Hupa territory had an average annual rainfall of 70.45 inches, and the Karuk territory 30.08 inches.

A total of 108 water samples and 48 field-rinse samples were collected and analyzed. None of the 32 herbicides or insecticides was detected above the reporting limit at any of the sampling sites. The reporting limits (reliable detection levels) for the analytical methods ranged from 0.04 to 2.0 ppb.

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DISCLAIMER

The mention of commercial products, their source, or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product

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INTRODUCTION

The Native Americans of northwestern California have voiced concerns over the use of pesticides and their potential impacts on the community and ecosystem health. These pesticides included herbicides used on private forestland for reforestation, on rights-of-way for weed management, and agriculture land for managing various pests. Some tribal people, particularly the Yurok, the Hupa, and the Karuk, who live in these rural forest communities rely on surface water for potable water source and as an important source of fish, wildlife and plant materials.

Reforestation practices particularly where fire or lumber harvest has resulted in large removal of harvestable timber generally include the use of herbicides. Herbicides are used to control the growth of unwanted vegetation prior to planting, during site preparation, and timber stand improvement following conifer establishment (Green and Cohn, 1982). In northwestern California, forestlands are characterized by extreme physiographic conditions with mountain areas that rise as high as 9,000 feet, with steep slopes and lithic makeup that are very susceptible to landslides (California Department of Forestry, 1979). In addition, the rainfall average ranges from 20 to 100 inches per year (Barrett, 1995). These conditions posed high potential for forestry herbicides to runoff. Monitoring studies have shown that herbicides such as hexazinone and triclopyr used in reforestation can be transported offsite in rain and/or snowmelt runoff (U.S. Forest Service, 1993; 1995). Another detailed study in two watersheds of the Klamath River showed that pesticide residues were present in agricultural drainages (Dileanis et al., 1996).

At the request of the Native American tribes in this region, the California Department of Pesticide Regulation (DPR), in collaboration with the U.S. Environmental Protection Agency's Office of Pesticide Programs conducted a one-year study to monitor surface waters for pesticide residues. The objective was to measure pesticide concentration at surface-water sites of importance to the tribes. Samples were taken during storm and irrigation runoffs under spatially and temporally worst-case scenarios.

MATERIALS AND METHODS

Study Sites

Sampling sites in each of the territories were selected based on their importance to the tribes, site accessibility, hydrology, and proximity to pesticide application. Three sites each were chosen for the Karuk and Hupa tribal territory. The sample sites encompassed three separate hydrologic areas (HA): Lower Trinity River HA, Middle Klamath River HA, and Scott River HA (Figures 1 and 2). Because of the significantly higher use of forestry herbicides and proximity of application in the Yurok territory, a separate monitoring study was conducted.

Table 1. Surface water sampling sites in the Karuk and Hupa Territories, Calif.

Site	Latitude and Longitude Coordinates (deg min sec)	Elevation (ft)
Klamath River at Horse Creek Bridge[a]	N 41 49 29 W 122 59 52	1785
Scott River at Hwy 96[a]	N 41 46 43 W 123 02 15	1545
Elk Creek[a]	N 41 46 50 W 123 23 36	1060
Pine Creek[a]	N 41 11 38 W 123 45 17	205
Supply Creek[b]	N 41 03 00 W 123 41 13	400
Trinity River at Tish Tang[b]	N 41 01 32 W 123 38 16	320

a. Lat/Long and elevation data from Trimble Geo*Explorer* GPS

b. Lat/Long and elevation data estimated from USGS 7.5 minute quad maps

In the Karuk territory, the Klamath River and Scott River sites were chosen because there has been documented forest herbicide and agricultural pesticide use upstream from them (DPR, 1998, 1999). In addition, Elk Creek was selected because of its importance as a domestic water supply, its accessibility, and its appreciable flow throughout the year.

In the Hupa territory, the Trinity River site was selected because there has been documented forest herbicide and general pesticide use upstream from the collection area (DPR, 1998, 1999). Supply and Pine Creeks were chosen because of their importance as fish spawning ground, domestic water supplies, accessibility, and their appreciable flow throughout the year.

Sampling Plan

From September 1998 to October 1999, sampling was conducted four times in both the Hupa and Karuk territories. The first sampling event in both territories was done under dry conditions, and served as background sampling. These samples were collected on September 23 and 30, 1998, in the Karuk and Hupa territories, respectively. Three subsequent sampling events followed on October 25, 1998, June 22, 1999, and October 28, 1999. The two sampling events in October 1998 and 1999 were coordinated with storm runoff events. The June 1999 sampling event corresponded with the end of the heaviest pesticide application season.

Composite water samples were collected using the equal-width increment method (SOP FSWA003.01; Appendix I). When this method was impractical at a site, a simpler depth-integrated grab or grab method was used. Equal-width increment and depth-integrated grab sampling was done from a bridge using a USGS D-77 sampler or in the water using a wading rod, each equipped with a 3-liter Teflon® bottle. Grab samples were taken using a clean 1-liter amber glass bottle attached to a 4.5-m aluminum extension pole by immersing the bottle upside down to a depth of approximately 1 m and then turning it to fill with water. Appropriate amounts of water were collected and poured into a stainless steel milk can for mixing. The sample mixture was then poured through a ten-port splitter (Geotech® Dekaport) into one-liter amber glass bottles to produce equal sample splits and sealed with Teflon®-lined caps (SOP FSWA004.00; Appendix I).

For the river sampling sites (Klamath, Scott, and Trinity Rivers), approximately 10 liters of water were collected and split into eight bottles to analyze for all 32 pesticides. One liter each was required for a) carbamate insecticides analysis, b) organophosphate insecticides analysis, c) diazinon analysis, d) phenoxy herbicides analysis, e) triazine/uracil/urea herbicides analysis, f) glyphosate analysis, g) acidified backup, and h) un-acidified backup.

For the creek sampling sites (Elk, Supply, and Pine Creeks), approximately five liters of water were collected and split into four bottles to analyze for 13 herbicides. One liter each was required for a) phenoxy herbicides analysis, b) triazine/uracil/urea herbicides analysis, c) glyphosate analysis, and d) un-acidified backup. Samples were stored on wet ice and predominantly maintained at 4^0C through storage and transportation to the laboratory until analysis (SOP QAQC004.01; Appendix 1). HOBO temperature gauges (SOP EQOT001.01; Appendix 1) were used and graphs showing readouts are kept on file.

Chemical Analysis

Water samples were analyzed for multiple substances at the six sampling sites. These substances can be categorized into five pesticide groups based on the chemical structural of each compound. These groups are the triazines/uracil/urea, phenoxys, organophosphates, carbamates, and miscellaneous. Individual pesticide compounds in these groups included the following:

Triazines/Uracil/Urea (TR): Atrazine, bromacil, diuron, cyanazine, hexazinone, metribuzin, prometon, prometryn, and simazine.

Phenoxys (PH): 2,4-D, MCPA, and triclopyr.

Organophosphates (OP): Azinphos-methyl, chlorpyrifos, DDVP, diazinon, dimethoate, ethoprop, fonofos, malathion, methidathion, methyl parathion, phosalone, phosmet, and phorate.

Carbamates (CB): Aldicarb, carbaryl, carbofuran, methiocarb, methomyl, and oxamyl.

Miscellaneous: Glyphosate (GL).

To preserve chemical constituents prior to analysis, the OP and CB samples were acidified to a pH range of 3.0 to 3.5 (SOP FSWA007.00, Appendix 1). Because diazinon breaks down rapidly at this pH, an additional sample was collected, and was not pH adjusted.

Pesticide analyses were performed by the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. The triazine herbicides were analyzed by both high performance liquid chromatography (HPLC) equipped with a UV detector and by GC equipped with a nitrogen phosphorus detector. The organophosphate insecticides were analyzed using gas chromatography (GC) equipped with a flame photometric detector. The carbamate insecticides were analyzed using HPLC, post column-derivatization and a fluorescence detector. The phenoxy herbicides were analyzed by GC on a capillary column using a mass selective detector. Glyphosate samples were analyzed using HPLC with a post column derivatization system. The

method validation recoveries are listed for each chemical in Appendix II. Detailed analytical methods, which contain reporting limits for each chemical in water, are included in Appendix III.

Quality Control

As part of our quality control (QC) program, data generated during method validation were used to assess all subsequent study results. The mean and standard deviation values from the validation data were used to establish warning and control limits at ±2s and ±3s, respectively, for each pesticide analysis (Appendix IV). Continuing QC samples consisted of water samples spiked with an analyte at a given concentration, extracted and analyzed with each extraction set. At the beginning of the study, only one matrix spike was required for each extraction set. Based on a recommendation made by the U.S. EPA's Quality Assurance Office, duplicate matrix spikes were required to assess laboratory precision at midway of the analysis (Taylor, 1998). During the course of the study, continuing QC samples were compared back to the warning and control limits. In addition, blind spikes were analyzed. A blind spike is a surface water sample that is spiked by one chemist and submitted to another for analysis.

As an additional quality assurance measure, field-rinse samples were prepared periodically after sample collection. In the field, all sampling equipment was cleaned with three de-ionized water rinses after each sampling event (SOP FSWA005.00; Appendix 1). Field-rinse samples were prepared by pouring de-ionized water into all sampling equipment after a typical cleaning procedure (SOP QAQC006; Appendix 1). These samples were then split into one-liter amber glass bottles, as was done for all water samples (SOP FSWA004.00; Appendix 1). Field-rinse samples were transported and stored with all other samples and were analyzed for all 32 compounds listed above. These samples served to determine if the sampling equipment was adequately cleaned.

Water Quality Measurements

Water quality measurements were made *in situ* at each sampling site, on each of the four sampling occasions. Water quality parameters measured *in situ* include water temperature, dissolved oxygen (DO), electrical conductivity (EC), and pH. These parameters were measured at each site, during each sampling event. Water temperature and EC were measured with an Orion® conductivity meter (model 142). DO was measured with an YSI (Yellow Springs Instruments) DO meter (model 58). Water pH was measured with a Sentron® pH meter (model 1001).

RESULTS AND DISCUSSION

Pesticide Residues

Physical and chemical properties of the herbicides and insecticides used are important to understanding how and why chemicals may or may not end up in surface waters. Solubility, half life and soil adsorption are some of the factors to be considered. In instances where there is a substantial period of time between applications and storm events, soil and field dissipation half-

lives are the critical properties to be considered. However, when the time elapsed between applications and storm events is short, solubility and soil adsorption are more critical. For example, many pesticides have high soil-adsorption coefficient (K_d) values (chlorpyrifos) that allow them to tightly bind to soil particles. Others, with low K_d values (hexazinone), are more likely to be found dissolved in water (Kollman and Segawa, 1995). In addition, the distance from the application to the sampling site (See Figures 4-10) is important, considering the chemicals ability for off-site transport by wind or runoff, and potential dilution along the way.

Pesticide Use Report

Table 2 is a summary of the herbicide and insecticide applications made in Humboldt, Siskiyou, and Trinity counties from June 1, 1998 to October 31, 1999. Of the 32 pesticides that were analyzed, only 14 were used within the three-county area during the sampling period.

A total of 40,631 lb of active ingredients was applied to the three counties that constitute most of the Klamath, Scott and Trinity River Basins. Of the herbicides applied, metribuzin was the most widely used, followed by hexazinone. Metribuzin was applied in a total of 264 separate applications. Ethoprop was the most heavily applied insecticide, with 12,498 lb. applied, but malathion was the most frequently used, in 96 separate applications. Most applications were made in Siskiyou county, with Humboldt and Trinity counties representing only a small percentage (7.0%).

Water Quality Measurements

Water quality measurements are shown in Table 3. The sample sites encompassed three separate hydrologic areas (HA): Lower Trinity River HA, Middle Klamath River HA, and Scott River HA. The North Coast Regional Water Quality Control Board has listed water quality guidelines for each of these areas (CRWQCB, North Coast region, 1994).

The guidelines for the Lower Trinity River HA, on the river (Trinity River @ Tish Tang) are DO above 8.0 mg/L, pH between 7.0 and 8.5, and EC below 275 µS/cm 90% of the time (90% Upper Limit) and below 200 µS/cm 50% of the time (50% Upper Limit). The guidelines for streams within the HA (Supply Creek) are DO above 9.0 mg/L, pH between 7.0 and 8.5, and EC below 250 µS/cm 90% of the time and below 200 µS/cm 50% of the time.

The guidelines for the Middle Klamath River HA, on the river (Klamath River @ Horse Creek) are DO above 8.0 mg/L, pH between 7.0 and 8.5, and EC below 350 µS/cm 90% of the time and below 275 µS/cm 50% of the time. The guidelines for streams within the HA (Pine and Elk Creeks) are: DO above 7.0 mg/L, pH between 7.0 and 8.5, and EC below 300 µS/cm 90% of the time and below 150 µS/cm 50% of the time.

The guidelines for the Scott River HA on the river are DO above 7.0 mg/L, pH between 7.0 and 8.5, and EC below 350 µS/cm 90% of the time and below 250 µS/cm 50% of the time. The plans do not provide any acceptable ranges for temperature, but the three HAs are designated as cold interstate water and their natural receiving water temperatures shall not be altered.

Water temperature measurements ranged from 10.3 to 22.8^{0}C and were within acceptable guidelines. pH ranged from 6.0 to 9.2. On one occasion, the pH value was below the minimum objective, and twice the pH was above maximum water quality guideline. Potential reasons for a high or low pH in natural waters include changes in carbonate equilibrium (Goldman and Horne, 1983) and pollution discharges. However, the reason for these values is not clear from the data collected.

Dissolved oxygen (DO) ranged from 7.01 to 10.68 mg/L, with one measurement below the guideline of 8.0 mg/L for the Middle Klamath HA. One potential explanation for a low DO is warmer water, but was not the case at the time of sampling. Electroconductivity (EC) ranged from 74 to 290 µS/cm, and was within the guideline for this parameter.

Rainfall

Due to the heavy annual rainfall within the study area, rain runoff from treated fields and timberlands is likely to flow into creeks and small watersheds that drain into the Klamath River Basin. Monthly rainfall data from six gauging stations, three in each territory, located across the study area for June 1, 1998 through October 31, 1999 are presented in Tables 4 and 6. Tables 5 and 7 show the daily rainfall for each month that sampling was done.

Rainfall averages in the Karuk Territory may be underestimated due to the elevation of the Collins Baldy and Fort Jones gauging stations, which may receive precipitation as snow rather than rain.

The two sampling events that took place in October 1998 and 1999 were coordinated with critical storm events of greater than 1.5 in (Tables 5 & 7). These were the first rain events after a long dry period, June through September, when considerable pesticide applications were made. Rainfall of that magnitude should be sufficient to produce runoff from agricultural fields and timberlands.

The river flow was also monitored at two sites. For the Trinity River, the Hoopa gauging station was used, which measures flow of the Trinity River at Hoopa. For the Klamath River, the Orleans gauging station was used, which measures flow of the Klamath River at Orleans. No flow data was available for the Scott River. In 1998, from October 24 to October 25 near the time of sampling, the Klamath River increased in flow from 3877 to 4800 cubic feet/second (cfs). Also, the river stage rose from 4.54 to 5.13 feet. During the same time, the Trinity River increased in flow from 628 to 1069 cfs, and the river stage rose from 11.51 to 12.34 feet. In 1999, from October 27 to October 28 near the time of sampling, the Klamath River increased in flow from 2798 to 6135 cfs, and the river stage rose from 4.21 to 6.49 feet. During the same time, the Trinity River increased in flow from 442 to 804 cfs, and the river stage rose from 11.33 to 12.19 feet (Department of Water Resources, California Data Exchange Center, 2000).

Chemical application in pounds of active ingredient and the average monthly rainfall in the two areas are presented in Figure 3. The heaviest rains during the study period were from November 1998 through March 1999. However, the heaviest applications occurred in the months following in April and May of 1999, which is to be expected.

Quality Control

All continuing QC sample results are listed in Appendix IV. Blind spike results are listed in Appendix V. For the triazine screen, a total of 64 spikes were analyzed during the study period. Of these, 54 were continuing QC spikes, and 10 were blind spikes. Of the 64-triazine spikes, four were recovered above the upper control limits, indicating that analytical results may over-estimate the concentrations about 6.25% of the time. Only one triazine spike fell below the lower control limit, indicating that analytical results may under estimate the actual concentrations about 1.5% of the time.

For the phenoxy screen, a total of 37 spikes were analyzed, with 10 of them being blind spikes. None of these spikes were recovered above or below the control limits. For glyphosate, 12 spikes were analyzed, five of which were blind spikes. Four of the glyphosate spikes were recovered above the upper control limit (33.3%). Of 74 organophosphate spikes, four of which were blind spikes, all were within the control limits. For the carbamate screen, 42 continuing QC spikes were analyzed, with one spike recovered above the upper control limit (2.4%). For diazinon, eight spikes were analyzed, two of which were blind spikes. All diazinon spikes were recovered within the control limits.

Out of the ten spikes that fell outside of the control limits, only one (10%) was below the lower limit. Therefore, our results tend to err high, not low, and are not expected to influence study conclusions. In certain instances, after being examined by DPR's Quality Assurance Officer, a backup sample was analyzed in order to verify sample results after spikes were recovered outside of their control limits.

Lastly, the 32 herbicides and insecticides analyzed for were not detected in the 48 field-rinse samples that were collected throughout the sampling period (Appendix VI).

CONCLUSION

A total of 108 water samples were collected and analyzed for a variety of herbicides and insecticides used within the study area. All of the samples contained no pesticide detections. Although applications were made throughout the study period and there is significant rainfall in the area, the heaviest applications were made during dry months. Therefore, prior to the rain, the chemicals may have time to degrade and/or adsorb to soil.

Due to the fact that applications are made all year round, combined with the heavy annual rainfall and steep topography in the area, the possibility of pesticide runoff due to storm events exists. However, timing and location of sampling events are difficult to determine. It is possible that by the time samples are collected, concentrations have been appreciably diluted and are no longer detectable.

Table 2. Summary of pesticide applications (lbs active ingredients) in the Humboldt, Siskiyou, and Trinity counties during 6/1/98 - 10/31/99.

month/year	Carbaryl	Chlorpyrifos	Malathion	Ethoprop	Aldicarb	Atrazine	Diuron	2,4-D	Metribuzin	Hexazinone	Triclopyr	Dimethoate	Phorate	Phosmet
Jun-98	365.2	157.0	108.3	550.0	--	--	--	222.0	106.9	--	233.3	--	--	5.6
Jul-98	--	--	1239.1	277.5	--	--	--	--	1359.4	1.0	--	--	--	--
Aug-98	--	--	1502.0	--	--	--	--	26.7	7.5	--	202.5	--	--	--
Sep-98	--	--	105.4	--	--	--	--	4.3	--	--	378.4	--	--	--
Oct-98	--	--	--	--	--	228.4	--	26.7	--	1163.3	88.7	--	--	--
Nov-98	--	--	--	--	--	--	--	--	--	537.5	--	--	--	--
Dec-98	--	--	--	--	--	--	--	--	--	--	--	--	--	1.0
Jan-99	--	--	--	--	--	--	474.7	--	34.9	321.8	--	--	--	--
Feb-99	--	--	--	--	--	--	32.5	--	54.4	161.7	--	--	--	--
Mar-99	--	--	--	--	--	--	790.0	--	1082.4	1842.7	--	--	--	--
Apr-99	--	1054.9	0.7	118.0	--	743.2	988.0	0.6	1259.6	1615.9	97.0	--	--	--
May-99	76.6	175.7	0.4	11552.9	351.0	--	150.2	--	92.6	59.9	--	--	--	--
Jun-99	--	--	0.5	--	--	--	--	176.4	1351.5	--	--	--	176.6	--
Jul-99	--	--	2456.5	--	--	--	--	1.9	666.9	--	--	24.01	--	--
Aug-99	--	--	2580.0	--	--	--	--	--	--	--	--	--	--	--
Sep-99	--	--	--	--	--	--	--	--	--	--	534.8	--	--	--
Oct-99	--	--	--	--	--	--	--	--	--	92.3	540.1	--	--	--
Total	441.7	1387.6	7992.7	12498.3	351.0	971.6	2435.4	458.7	6016.2	5796.0	2074.7	24.01	176.6	6.6

Table 3. Water quality measurement at surface water sampling sites.

Site	Date	Temperature (^{0} C)	pH	Dissolved Oxygen (DO) (mg/L)	Electroconductivity EC (µS/cm)
Klamath River @ Horse Creek	9/23/98	18.5	8.9	*	196
	10/25/98	--	--	--	--
	6/22/99	18.0	7.9	8.28	207
	10/28/99	12.3	7.7	7.01	214
Scott River	9/23/98	16.6	9.2	*	290
	10/25/98	--	--	--	--
	6/22/99	15.0	8.1	8.80	106**
	10/28/99	10.3	8.1	8.62	271
Elk Creek	9/23/98	14.9	6.0	*	179
	10/25/98	--	--	--	--
	6/22/99	16.7	7.8	9.20	86**
	10/28/99	*	7.4	8.70	120
Pine Creek	9/30/98	14.4	8.5	9.10	119
	10/25/98	11.1	7.5	10.45	106
	6/22/99	17.4	7.6	9.60	74
	10/28/99	11.3	7.7	10.65	103
Supply Creek	9/30/98	14.9	8.4	9.34	197
	10/25/98	11.4	7.5	10.45	187
	6/22/99	16.5	7.8	9.45	159
	10/28/99	11.1	8.0	10.68	177
Trinity River @ Tish Tang	9/30/98	17.8	8.3	8.74	157
	10/25/98	13.5	7.3	10.02	179
	6/22/99	22.8	7.9	8.40	115
	10/28/99	12.7	8.0	10.51	178

-- Data not available

* No measurement taken due to faulty meter

** Measurement taken at West Sacramento warehouse facility

Table 4. Monthly rainfall (inch) at three gauging stations representing the Hoopa sampling area.

Date	Hoopa[a]	Orleans[b]	Willow Creek[c]	Average
Jun-98	0.04	0.03	0.00	0.02
Jul-98	0.00	0.00	0.00	0.00
Aug-98	0.00	0.00	0.00	0.00
Sep-98	0.24	0.12	0.16	0.17
Oct-98	3.60	3.44	2.04	3.03
Nov-98	22.24	18.32	16.97	19.18
Dec-98	6.60	6.00	6.47	6.36
Jan-99	12.04	10.04	10.01	10.70
Feb-99	19.80	18.00	15.01	17.60
Mar-99	6.64	5.88	10.88	7.80
Apr-99	1.56	1.60	2.60	1.92
May-99	0.80	0.84	0.81	0.82
Jun-99	0.00	0.00	0.00	0.00
Jul-99	0.00	0.00	0.00	0.00
Aug-99	0.20	0.28	0.33	0.27
Sep-99	0.00	0.00	0.00	0.00
Oct-99	2.56	3.08	2.19	2.61

a. Hoopa gauging station, Elev. 330 ft. (data obtained from CDEC)

b. Orleans gauging station, Elev. 430 ft. (data obtained from CDEC)

c. Willow Creek gauging station, Elev. 460 ft. (data obtained from Lower Trinity Ranger District, Six Rivers NF)

Table 5. Daily rainfall for the months of each sampling event in the Hoopa territory.

Date	Hoopa	Orleans	Willow Creek	Average
9/27/98	0.24	0.12	NA	0.18
9/28/98	---	---	0.15	0.05
9/30/98	---	---	---	---
10/2/98	0.04	0.04	---	0.03
10/7/98	0.24	0.24	---	0.16
10/8/98	0.52	0.56	0.15	0.41
10/9/98	---	---	0.1	0.03
10/12/98	0.36	0.44	---	0.27
10/13/98	0.16	0.08	0.35	0.20
10/24/98	1.64	1.40	NA	1.52
10/25/98	---	---	NA	---
6/22/99	---	---	---	---
10/5/99	NA	0.04	---	0.02
10/6/99	---	0.08	0.16	0.08
10/26/99	0.20	0.36	---	0.19
10/27/99	1.68	1.84	0.28	1.27
10/28/99	0.68	0.76	1.75	1.06

--- = No measurable precipitation; NA = Not Available

BOLD = day of sampling event

Table 6. Monthly rainfall (in) at three gauging stations representing the Karuk sampling area.

Date	Collins Baldy[a]	Fort Jones[b]	Happy Camp[c]	Average
Jun-98	0.91	0.41	0.20	0.51
Jul-98	0.63	0.17	0.03	0.28
Aug-98	0.00	0.00	0.00	0.00
Sep-98	0.13	0.13	0.00	0.09
Oct-98	0.77	1.05	2.64	1.49
Nov-98	2.51	8.90	9.24	6.88
Dec-98	0.08	1.36	5.20	2.21
Jan-99	0.48	4.70	8.61	4.60
Feb-99	0.60	7.80	15.98	8.13
Mar-99	0.14	1.01	8.55	3.23
Apr-99	0.11	0.19	1.80	0.70
May-99	0.04	0.07	0.33[d]	0.15
Jun-99	0.00	0.01	0.00	0.00
Jul-99	0.02	0.00	0.00	0.01
Aug-99	0.79	0.46	0.64	0.63
Sep-99	0.00	0.00	0.00	0.00
Oct-99	1.11	1.07	3.72	1.97

a. Collins Baldy gauging station, Elev. 5493 ft. (data obtained from CDEC)

b. Fort Jones gauging station, Elev. 2725 ft. (data obtained from Fort Jones Ranger Station)

c. Happy Camp gauging station, Elev. 1120 ft. (data obtained from Happy Camp Ranger Station)

d. Data obtained from CDEC

Table 7. Daily rainfall for the months of each sampling event in the Karuk territory.

Date	Collins Baldy	Fort Jones	Happy Camp	Average
9/23/98	---	---	---	---
10/1/98	0.01	---	---	---
10/2/98	0.02	0.04	0.07	0.04
10/7/98	0.01	---	---	---
10/8/98	0.13	0.28	0.71	0.37
10/12/98	0.04	NA	NA	0.04
10/13/98	0.06	0.21	0.44	0.24
10/14/98	0.02	0.03	0.23	0.09
10/24/98	0.14	NA	NA	0.14
10/25/98	---	NA	NA	---
6/16/99	---	0.01	---	---
6/22/99	---	---	---	---
10/6/99	0.02	---	0.15	0.06
10/7/99	---	0.01	---	---
10/26/99	0.18	---	0.02	0.07
10/27/99	0.80	0.18	0.37	0.45
10/28/99	0.11	0.88	3.18	1.39

--- = No measurable precipitation; NA = Not Available

BOLD = day of sampling event

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U.S. Forest Service. 1995. Water monitoring report: 1993 herbicide application projects, El Dorado National Forest. U.S. Department of Agriculture. Placerville, California.

Figure 1. Karuk Monitoring Sites in the Lower Klamath River Drainage Basin.

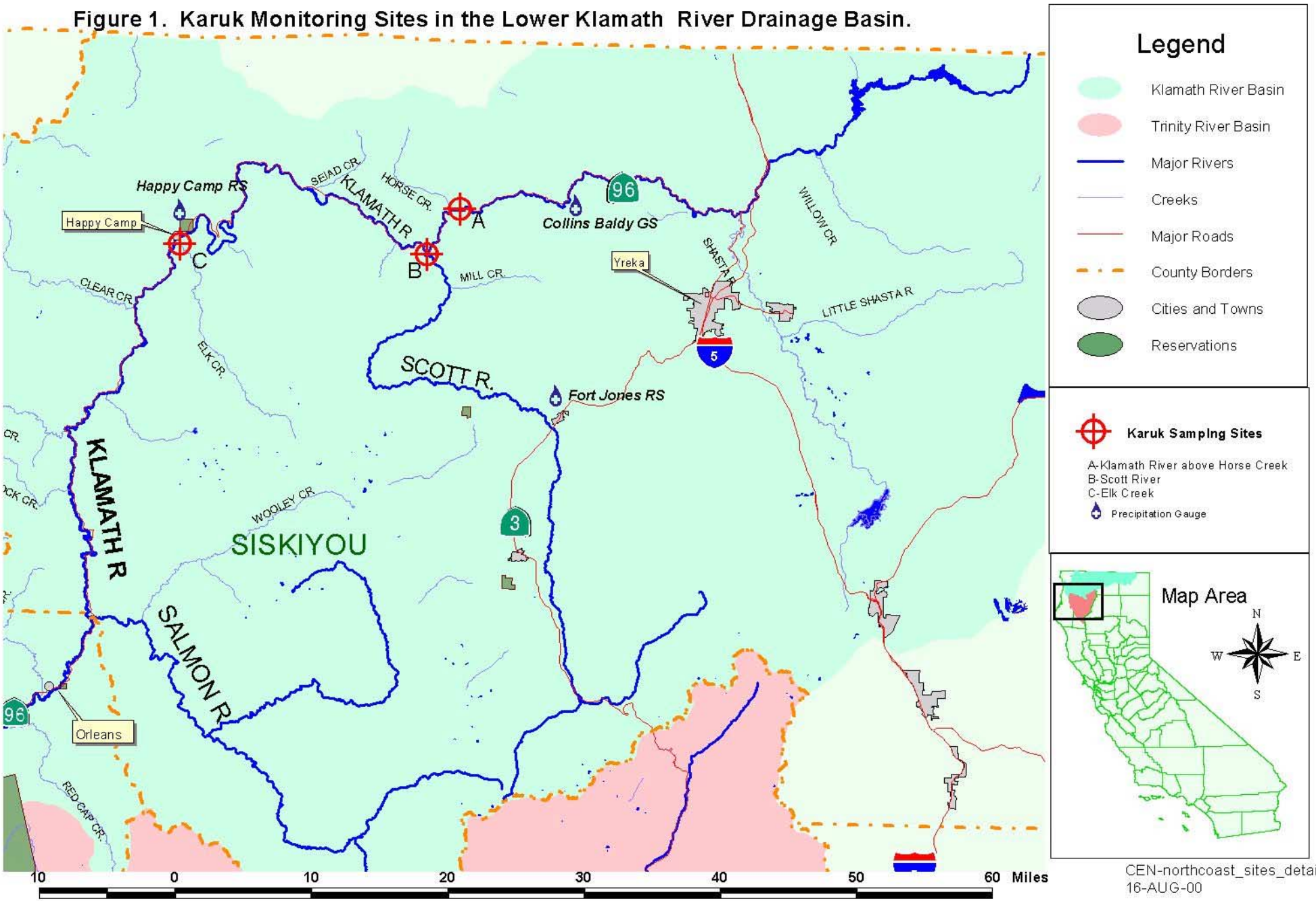

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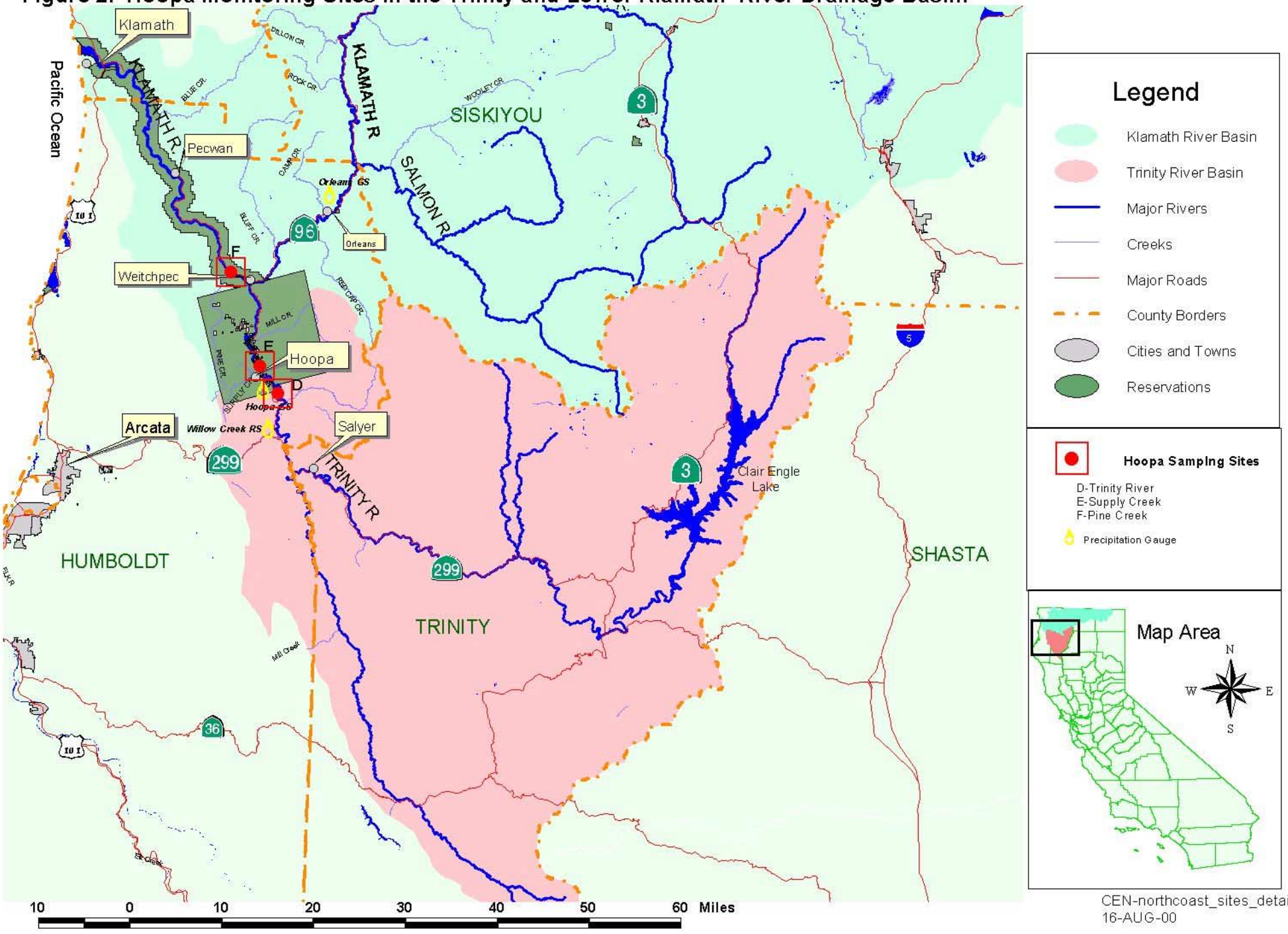
Figure 2. Hoopa Monitoring Sites in the Trinity and Lower Klamath River Drainage Basin.



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16-AUG-00

Figure 3. Pounds of active ingredient applied and rainfall averages in the study area

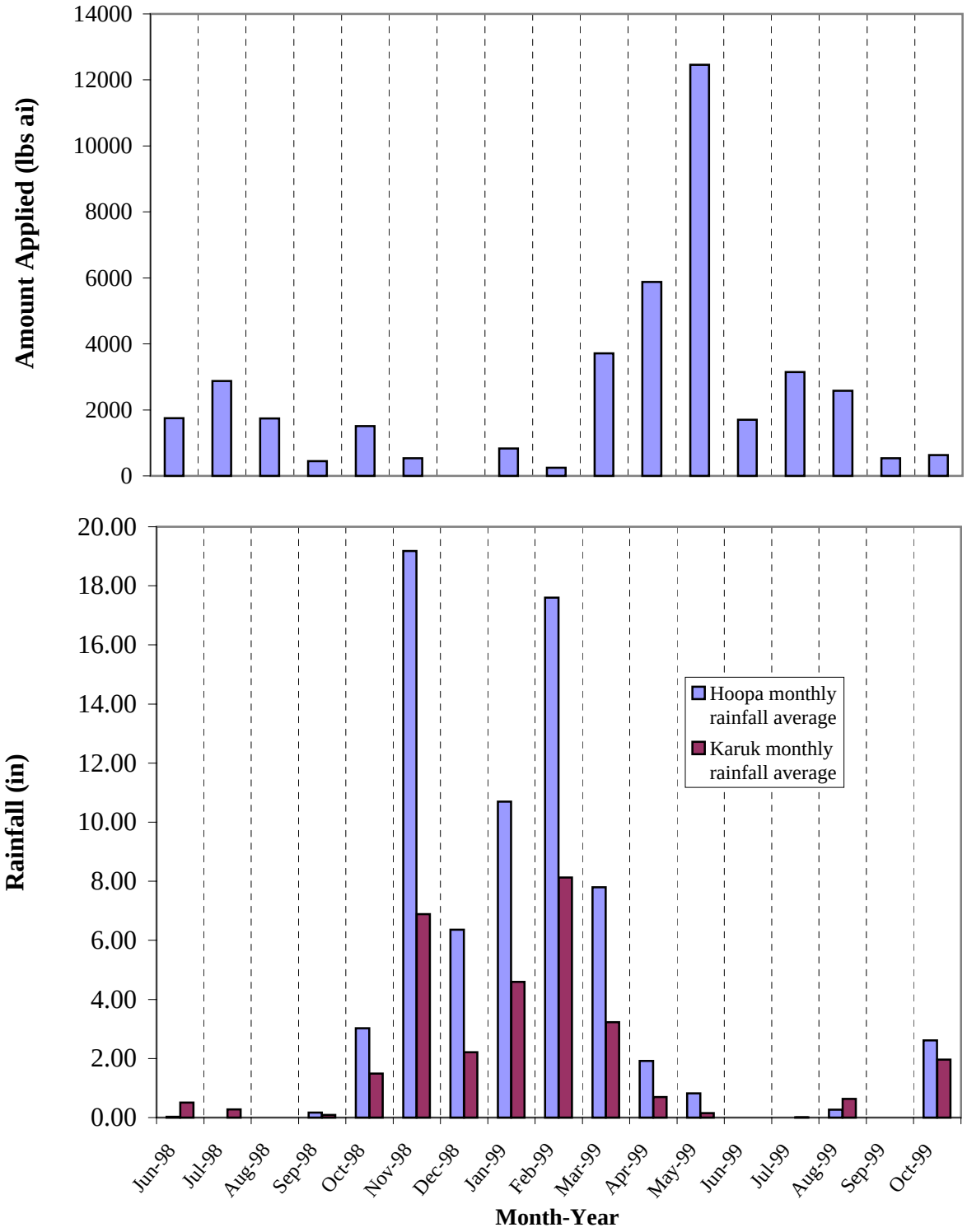


Figure 4. Metribuzin and Triclopyr in the Klamath and Trinity River Basins, 1 June 1998 to 31 October 1999

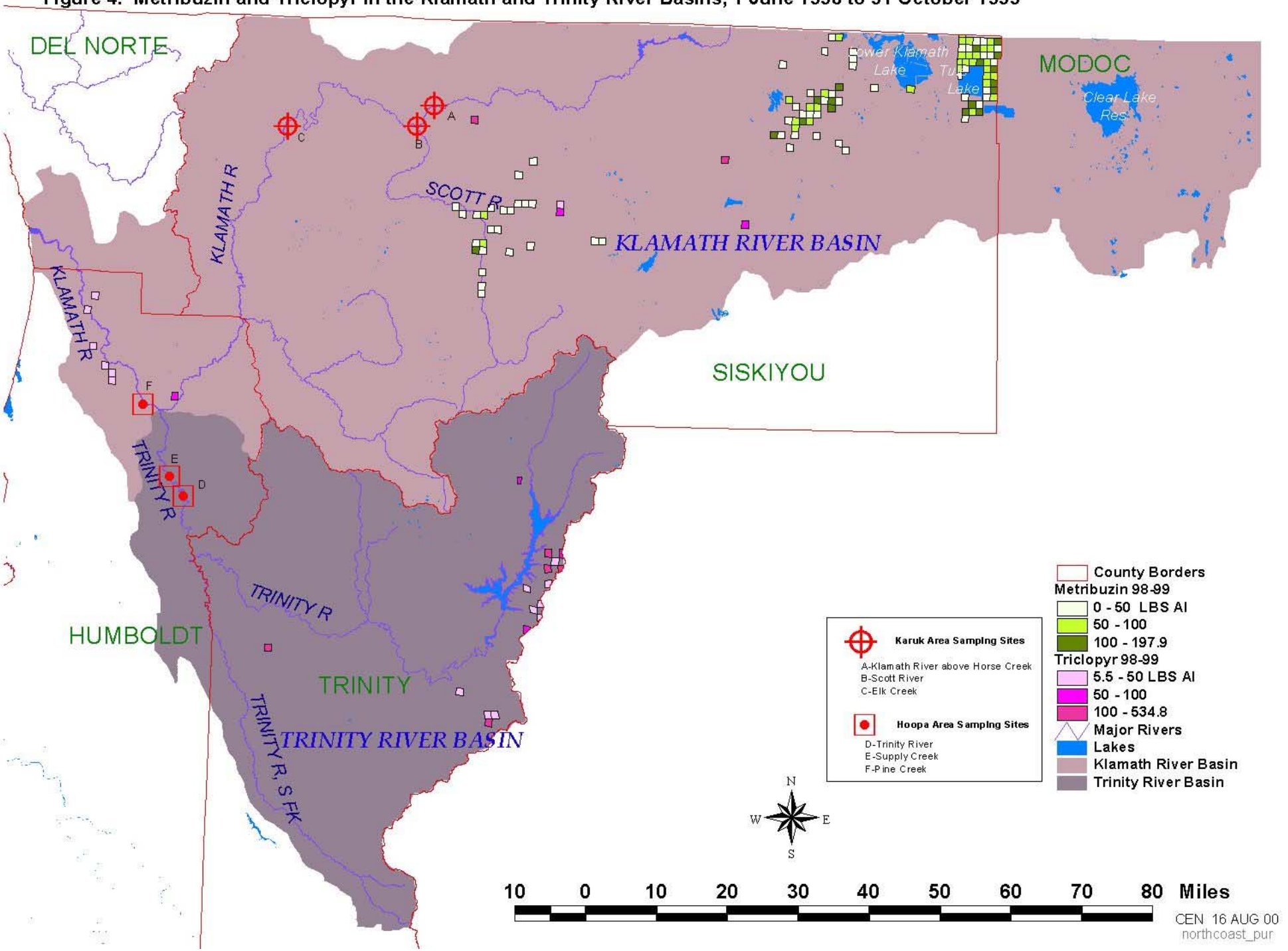


Figure 5. 2,4-D, Atrazine, and Diuron in the Klamath and Trinity River Basins, 1 June 1998 to 31 October 1999.

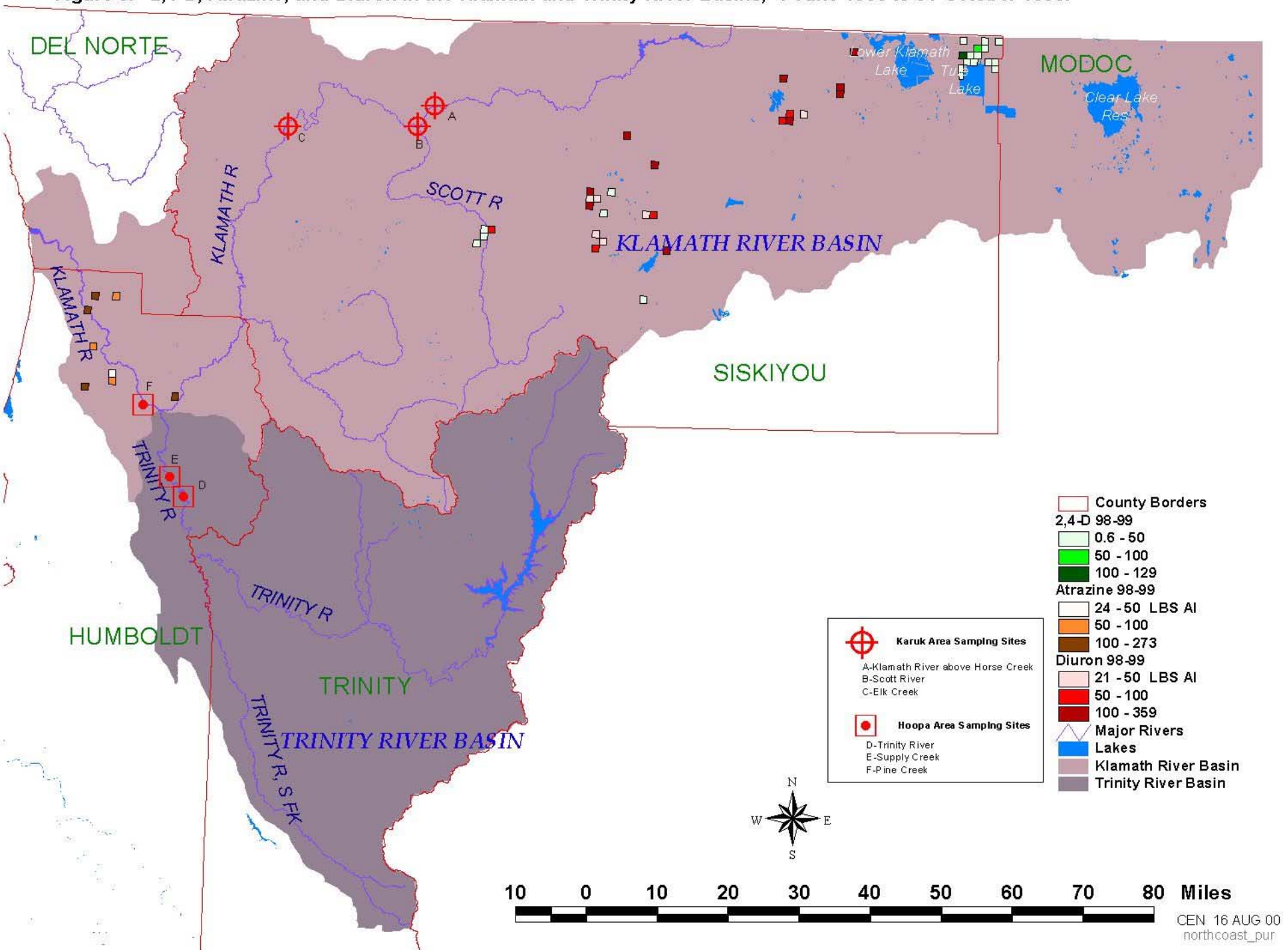


Figure 6. Combined Use of the Insecticides: Aldicarb, Carbaryl, Chlorpyrifos, Dimethoate, Ethoprop, Malathion, Phorate, and Phosmet, in the Klamath and Trinity River Basins, 1 June 1998 to 31 October 1999

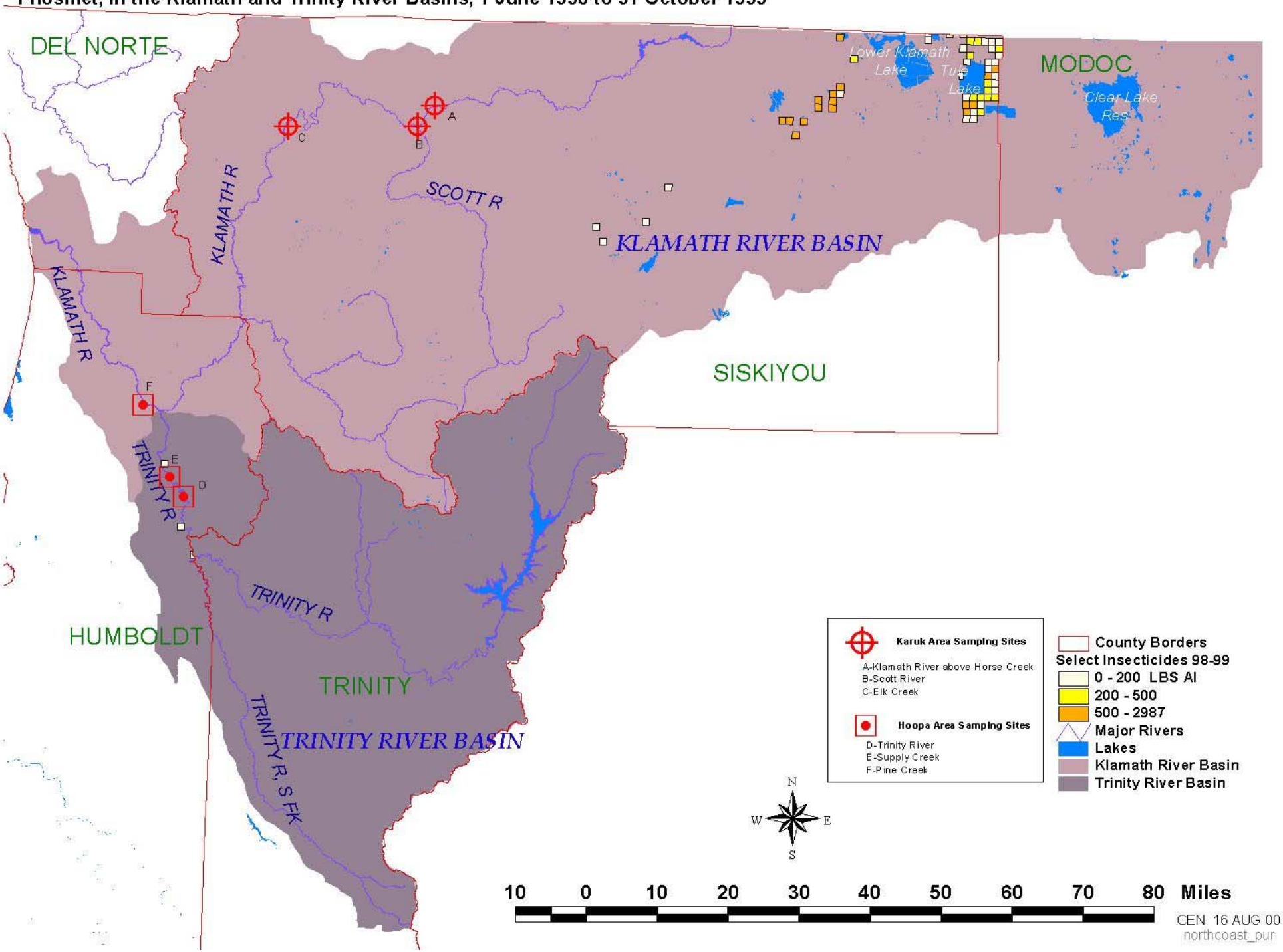
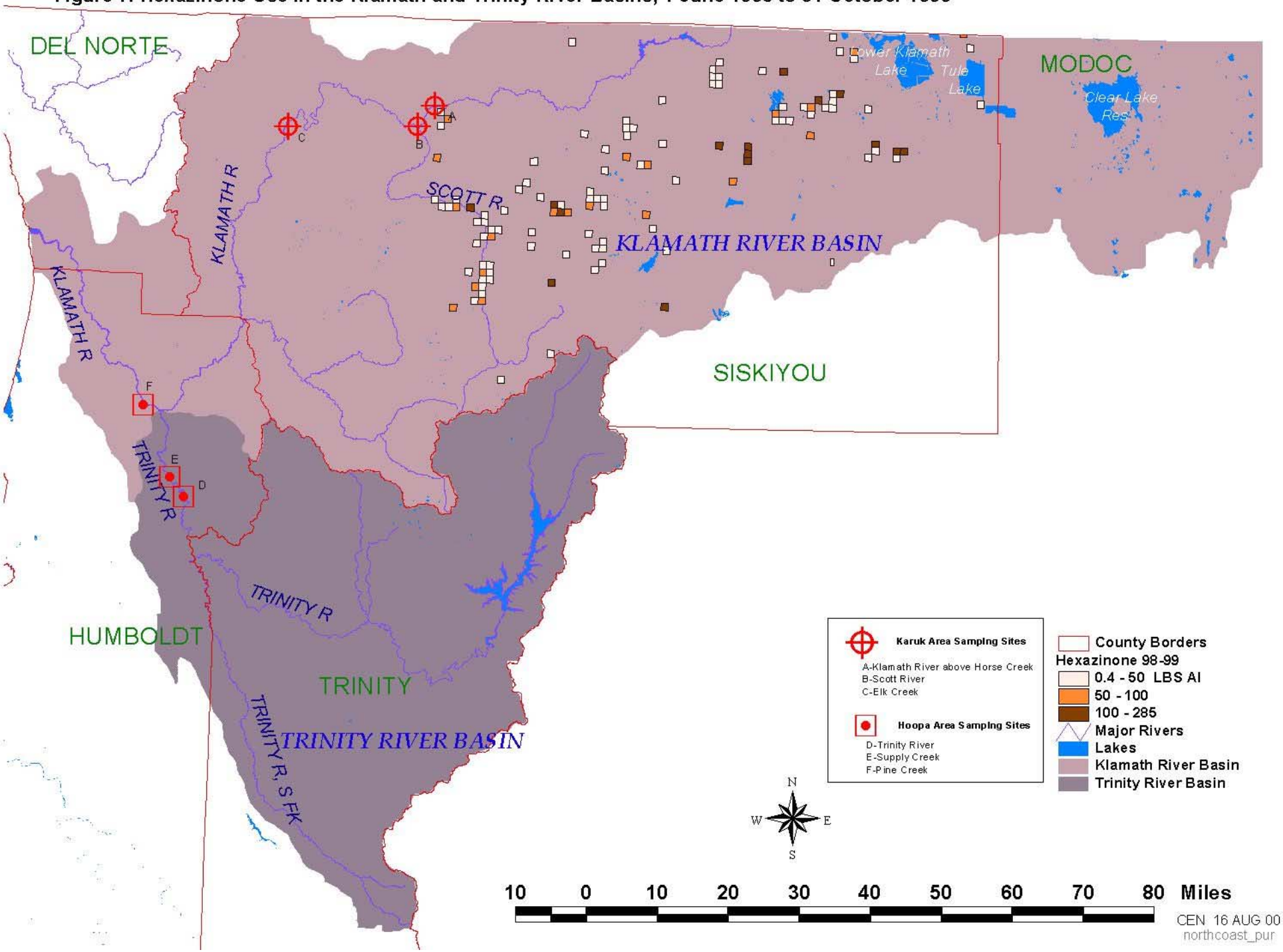


Figure 7. Hexazinone Use in the Klamath and Trinity River Basins, 1 June 1998 to 31 October 1999



STUDY ~~FIELD ID~~ NO: 170

S.D. NAN SINGHASEMANON

FIELD DATA BOOK

PART 1. GOOD LABORATORY PRACTICE COMPLIANCE INFORMATION

E. QUALITY ASSURANCE INSPECTION STATEMENT

THIS PAGE IS TO BE COMPLETED AND SIGNED BY THE QUALITY ASSURANCE UNIT

1. THIS RESEARCH TRIAL UNDERWENT A QUALITY ASSURANCE AUDIT AND/OR INSPECTION FOR GLP COMPLIANCE ON THE FOLLOWING DATE(S)

DATE	EVENT/PHASE AUDITED	AUDITOR	DATE FINDINGS REPORTED (SENT) TO: STUDY DIRECTOR AND MANAGEMENT
7/8/98	PROTOCOL SIGNED	C Ganapathy	PROTOCOL REVIEWED PREVIOUSLY W/CORRECTIONS SENT TO NAN S.
6/22/99	Field portion Audit.	C Ganapathy	7/7/99 sent to Nan
10/29/99	Warehouse inspection	C. Ganapathy	10/22/99 sent to Nan
11/3/99	COFA lab inspection	C. Ganapathy	11/22/99 sent to Nan
10/28/00 (18 CA)	Report Reviewed	C. Ganapathy	10/26/00 (19 CA) sent to Kean
10/30/00	Facility inspection DPR Protn. + Pre-archive review	C. Ganapathy	10/30/00 sent to Dee Jones + Copy to K. Goh

2. HAS A TRIAL SITE FACILITY INSPECTION FOR GLP COMPLIANCE BEEN PERFORMED WITHIN THE LAST 12 MONTHS?

X YES, IF YES GIVE DATE OF FACILITY INSPECTION: 10/29/99

____ NO

Pursuant to Good Laboratory Practice Regulations (40 CFR 160), this statement verifies that the aforementioned study was inspected and/or audited and the findings reported to the Study Director and to Management by the QAU on the dates listed above.

(Signature): Carissa Ganapathy

Print Name: CARISSA GANAPATHY

Date: 10/30/00

3971 COMMERCE DR W. SACTO

Address/Phone (916) 322-3082.

STUDY
~~FIELD ID~~ NO: 171
S.D. NAN SING HASEMANON

FIELD DATA BOOK

PART 1. GOOD LABORATORY PRACTICE COMPLIANCE INFORMATION

E. QUALITY ASSURANCE INSPECTION STATEMENT

THIS PAGE IS TO BE COMPLETED AND SIGNED BY THE QUALITY ASSURANCE UNIT

1. THIS RESEARCH TRIAL UNDERWENT A QUALITY ASSURANCE AUDIT AND/OR INSPECTION FOR GLP COMPLIANCE ON THE FOLLOWING DATE(S)

DATE	EVENT/PHASE AUDITED	AUDITOR	DATE FINDINGS REPORTED (SENT) TO: STUDY DIRECTOR AND MANAGEMENT
9/10/98	Protocol SIGNED	CGana	PROTOCOL REVIEWED PREVIOUSLY W/CORRECTIONS SENT TO NANS.
6/22/99	field Audit on study 170*	CGana	6 7/7/99 to Nan
10/29/99	Warehouse inspection	CGana	11/22/99
11/3/99	CDFA lab inspection	CGana	11/22/99
10/18/00	Report Reviewed	CGana	10/19/00 sent to Kean.
10/30/00	FACILITY INSPECTION OF DPR OFFICE AND PRE-ARCHIVE REVIEW.	CGana	10/30/00 sent to D. Jones Copy to K. Goh.

2. HAS A TRIAL SITE FACILITY INSPECTION FOR GLP COMPLIANCE BEEN PERFORMED WITHIN THE LAST 12 MONTHS?

X YES, IF YES GIVE DATE OF FACILITY INSPECTION: 10/29/99
___ NO

Pursuant to Good Laboratory Practice Regulations (40 CFR 160), this statement verifies that the aforementioned study was inspected and/or audited and the findings reported to the Study Director and to Management by the QAU on the dates listed above.

(Signature): Carissa Ganapathy

Print Name: CARISSA GANAPATHY
Date: 10/30/00

3971 COMMERCE DR.
W. SACTO CA 95691
Address/Phone (916) 322-3082

* Conducted at the same time as 171 in different region. followed same sampling methods.

APPENDIX I
Standard Operating Procedures

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE
Personnel Organization and Responsibilities for Studies

KEY WORDS

management; project supervisor; project leader; senior scientist; field coordinator; quality assurance officer; laboratory liaison; statistician; chemist; contact person; GLP; safety; problem resolution

APPROVALS

APPROVED BY: John L. Sanders — DATE: 3/6/97
Management

APPROVED BY: K L Bro — DATE: 3-5-97
EHAP Senior Scientist

APPROVED BY: Randy Segawa — DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: Randy Segawa — DATE: 2-26-97

No previous SOP exists; however, this SOP does supersede the following policy memos:

Goh, K.S. Responsibilities of Field Coordinator for EHAP studies. Memorandum to EHAP Personnel, dated 9/24/93.

Sanders, J. Responsibilities of Project Leaders Regarding Chemical Analysis. Memorandum to EHAP Staff, dated 6/13/88.

Sanders, J. Lab Liaison Personnel and Policy. Memorandum to EHAP Personnel, dated 7/1/87.

STANDARD OPERATING PROCEDURE
Personnel Organization and Responsibilities for Studies

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) defines and discusses the organization and responsibilities of personnel for Environmental Hazards Assessment Program (EHAP) studies. This SOP primarily applies to EHAP field studies, but can also apply to non-field projects.

1.2 Definitions

1.2.1 **Branch** refers to an organizational unit within the Department of Pesticide Regulation (DPR). There are six branches within DPR as shown in Figure 1.

1.2.2 **Protocol** refers to a written document that describes the objectives, personnel, study design, sampling procedures, analytical procedures, data analysis, and schedule for a specific study.

1.3 EHAP Organization

The EHAP is a unit within the Department of Pesticide Regulation (DPR) and provides technical support and monitoring regarding the environmental fate of pesticides. The department and organization of program personnel are shown in Figure 1.

2.0 STUDY ORGANIZATION

Figure 1 shows that the EHAP is organized into groups by function or technical specialty. Personnel are organized into a team for each study. Key study personnel include the Management, Project Supervisor, Project Leader, Senior Scientist, Field Coordinator, Laboratory Liaison, Quality Assurance Officer, Statistician, Chemist and Contact Person. The personnel listed above may not be included in all studies. With certain restrictions, the duties of two or more people may be performed by one person (e.g., the duties of the Project Supervisor and Project Leader may be performed by a single person). The most common personnel organization for a study is shown in Figure 2. The Project Supervisor is selected by the branch chief and/or program supervisor. The Project Leader and other team members are selected by the program supervisor and group supervisors. Selection of all team members should be made

early in the developmental stages of a study to allow them time to understand what management wants to accomplish and to allow sufficient time to prepare for implementing the study.

3.0 PERSONNEL RESPONSIBILITIES

The following personnel have specific responsibilities when assigned to a study.

3.1 Management - Management typically consists of the Assistant Director and Branch Chief and sometimes the Program Supervisor. Management has responsibility for all policy issues, includng the following:

- 3.1.1 determines the objective of a study
- 3.1.2 selects the project supervisor
- 3.1.3 gives final approval for the study protocol, including the budget
- 3.1.4 gives final approval for all SOPs
- 3.1.5 gives approval to any changes in finalized protocols
- 3.1.6 sets study deadlines
- 3.1.7 gives final approval for the study report and any interim memos

3.2 Project Supervisor - The Project Supervisor is typically the supervisor of the Project Leader (i.e., a senior environmental research scientist (supervisor) or the Program Supervisor). The Project Supervisor has overall responsibility for the administrative and technical aspects of the study, including the following:

- 3.2.1 refines the study objectives
- 3.2.2 selects the Project Leader
- 3.2.3 gives general direction to the Project Leader
- 3.2.4 acts as editor-in-chief for review of documents (e.g. protocol, memos, SOPs, report)
- 3.2.5 reviews and approves any changes in finalized protocols
- 3.2.6 supervises administrative tasks (e.g., contracts, purchases, hires)
- 3.2.7 supplies personnel and resources to the Project Leader
- 3.2.8 establishes responsibilities of each team member - consulting with Project Leader
- 3.2.9 facilitates communication with other groups and other branches
- 3.2.10 responsible for safety - determines safety procedures and disseminates hazard communication information - consulting with other DPR branches
- 3.2.11 helps resolve scientific differences of opinion

If the study is conducted under Good Laboratory Practices (GLP), the Project Supervisor is assigned to Management and is also responsible for the following:

3.2.12 establishes a quality assurance unit
3.2.13 assures that test and control substances or mixtures have been tested for identity, strength, purity, stability and uniformity
3.2.14 assures that any deviations from GLP are communicated to the Study Director (Project Leader) and corrective actions are taken and documented

3.3 Project Leader - The Project Leader is typically an environmental research scientist (ERS), associate ERS, or a senior ERS. The Project Leader has primary responsibility for all technical aspects of a study, including the following duties. Some of the following responsibilities may be delegated to other team members.

3.3.1 gathers background information for study - conducts literature search, gathers pesticide use data
3.3.2 identifies personnel needs - sampling, chemical analysis, data analysis
3.3.3 formulates study plan after consulting with team members
3.3.4 writes and follows study protocol and any changes
3.3.5 coordinates protocol dissemination with contact person
3.3.6 communicates with study cooperators - growers, agencies
3.3.7 specifies lab goals through lab liaison - methodology, validation, reporting limits, quality control, turnaround time
3.3.8 interacts with interested parties through the contact person - agencies, public
3.3.9 develops chain of custody form - consults with team members
3.3.10 conducts administrative tasks - contracts, timesheets, purchases, services, budget, expenditures tracking
3.3.11 documents all study activities
3.3.12 obtains necessary permits
3.3.13 determines sampling methodology - consulting with team members
3.3.14 determines sampling schedule - consulting with field coordinator
3.3.15 prepares all pertinent SOPs
3.3.16 trains personnel in study tasks
3.3.17 supervises field sampling and/or data collection
3.3.18 arranges for special facilities - storage, experimental plots
3.3.19 determines sample priorities for lab analysis

3.3.20 reviews and accepts data from the lab
3.3.21 designates samples for reanalysis
3.3.22 reviews laboratory SOPs
3.3.23 supervises data analysis
3.3.24 writes interim progress reports or memos
3.3.25 writes final report - with other team members
3.3.26 coordinates report dissemination with contact person
3.3.27 archives study data
3.3.28 presents results to various audiences

If the study is conducted under GLP, the Project Leader is designated as the Study Director and is also responsible for the following:

3.3.29 corrective actions are taken and documented when necessary
3.3.30 GLP requirements are followed

3.4 Senior Scientist - The Senior Scientist is typically a senior ERS (specialist). The duties of the Senior Scientist and Project Leader cannot be performed by a single person. The Senior Scientist reviews and approves a study for scientific adequacy, including the following specific duties:

3.4.1 gives technical advice to the Project Leader
3.4.2 reviews and approves protocols, memos, SOPs (including lab SOPs) and reports for scientific adequacy
3.4.3 helps resolve scientific differences of opinion
3.4.4 reviews and approves revisions to protocols and SOPs
3.4.5 reviews and approves final report

If the study is conducted under GLP, the Senior Scientist is assigned to the Quality Assurance Unit and assists the Quality Assurance Officer.

3.5 Field Coordinator - The Field Coordinator is typically an associate ERS, ERS, or environmental research assistant from one of the field groups. The Field Coordinator oversees the collection of field samples and has responsibility for field safety. He/She may have more or fewer duties depending on the preference of the Project Supervisor and Project Leader. The Field Coordinator will normally act for the Project Leader in the Project Leader's absence. More than one Field Coordinator may be assigned for very complex studies. The Field Coordinator is normally responsible for the following duties:

3.5.1 decides safety issues under direction of Project Supervisor - the Field Coordinator has the authority to modify or terminate any field activity which threatens the health or safety of field personnel; provides or arranges for safety training
3.5.2 assembles sampling materials
3.5.3 purchases needed materials
3.5.4 arranges transportation and housing
3.5.5 checks and calibrates equipment
3.5.6 assists in developing chain of custody format
3.5.7 assists in coordinating activities with study cooperators
3.5.8 assists in selecting sampling sites
3.5.9 gives advice on sampling methodology
3.5.10 assists in the preparation of SOPs
3.5.11 recommends personnel needs and sampling schedule
3.5.12 prepares sampling materials list
3.5.13 collects and transports samples
3.5.14 coordinates sampling schedule with the Lab Liaison
3.5.15 cleans sampling materials
3.5.16 supervises field sampling in the absence of the Project Leader
3.5.17 assists in the protocol preparation
3.5.18 assists in the report preparation

3.6 Quality Assurance Officer - The Quality Assurance Officer is typically an associate ERS. Duties of the Quality Assurance Officer and Laboratory Liaison are typically performed by one person. The Quality Assurance Officer cannot perform the duties of the Project Leader or Field Coordinator. The Quality Assurance Officer is responsible for documentation and the quality of the laboratory analysis, including the following specific duties:

3.6.1 assists the Project Leader in specifying laboratory methodology
3.6.2 assists the Project Leader in specifying laboratory quality control procedures
3.6.3 reviews and approves EHAP SOPs
3.6.4 maintains copies of protocols and EHAP SOPs
3.6.5 reviews, compiles and disseminates quality control data
3.6.6 notifies Project Leader of analytical problems
3.6.7 initiates lab corrective actions - consulting with Project Leader
3.6.8 arranges the preparation of quality control samples

3.6.9 resolves lab discrepancies
3.6.10 produces method validation and quality control tables for the report
3.6.11 obtains and disseminates laboratory SOPs
3.6.12 reviews laboratory SOPs

If the study is conducted under GLP, the Quality Assurance Officer supervises the Quality Assurance Unit and is responsible for the following:

3.6.13 maintains master schedule of EHAP GLP studies
3.6.14 determines that all known deviations from the protocol or SOPs were authorized and documented
3.6.15 prepares and signs statement of dates of inspection and findings to be included in final report
3.6.16 reviews and approves protocol and final report

3.7 Laboratory Liaison - The Laboratory Liaison is typically an associate ERS. Duties of the Laboratory Liaison and Quality Assurance Officer are typically performed by one person. The Laboratory Liaison is responsible for coordinating activities between EHAP and the chemistry labs, including the following duties:

3.7.1 acts as liaison between the Project Leader and the labs
3.7.2 selects the chemistry laboratories (primary and quality control)
3.7.3 negotiates analytical specifications with the labs (described in SOP QAQC001)
3.7.4 stores and transports samples to the labs
3.7.5 controls timing and quantity of samples delivered to the lab
3.7.6 tracks movement of samples between storage facility and lab
3.7.7 transmits lab data to the Project Leader
3.7.8 administers lab contracts

3.8 Chemist - The Chemist typically works for the Department of Food and Agriculture or a commercial lab, not EHAP. The Chemist is responsible for the pesticide analysis of samples. He/she also gives advice on sampling methodology.

3.9 Statistician - The Statistician is typically an associate ERS. The Statistician is responsible for the design and statistical analysis of the study, including the following specific duties:

3.9.1 determines the study design - consulting with other team members
3.9.2 assists in writing the protocol

3.9.3 reviews and approves the study protocol and any changes
3.9.4 conducts statistical analysis of the study data
3.9.5 assists in writing the final report
3.9.6 reviews final report

3.10 Contact Person - The Contact Person is typically assigned from Program Representation of the Environmental Monitoring Branch. The Contact Person acts as liaison with the public, branches, and agencies that are interested but not participants in the study. His/Her specific duties include the following:

3.10.1 develops interested parties list - consulting with the Project Leader
3.10.2 acts as liaison to public/branches/agencies
3.10.3 disseminates appropriate documents to interested parties
3.10.4 coordinates review of documents with interested parties
3.10.5 assists the DPR communications office with media inquiries
3.10.6 writes executive summary
3.10.7 advises Project Leader on policy and regulatory issues of study

3.11 Other EHAP and DPR Personnel - Designated personnel provide support services. EHAP warehouse personnel provide storage, maintenance, equipment and transportation upon request. EHAP laboratory facilities are available for soil characterization and other analyses upon request. A number of people within and outside of EHAP provide special computer services such as programs, databases, modeling, geographic information systems, or graphics upon request. The Worker Health and Safety, and Medical Toxicology Branches can provide information on toxicity, safety precautions as well as medical monitoring upon request. These support personnel may not be available for all studies and should be requested through the Project Supervisor or the appropriate Group Supervisor.

4.0 PROBLEM RESOLUTION

Technical items that are not specified here are the responsibility of the Project Leader. Both the Project Leader and Senior Scientist should agree on all technical issues. The Project Supervisor is responsible for resolving any disagreements. Administrative, policy or other items not specified here are the responsibility of the Project Supervisor.

5.0 SAFETY

Personnel safety is of primary importance at all times. The Project Supervisor and Field Coordinator have primary responsibility for safety. However, all team members must follow correct safety procedures. Approval for changing the protocol or a SOP should be sought whenever possible, but may not be possible if an imminent danger exists. A study should always be conducted in a safe manner, no matter what the protocol or SOP specifies. Document all changes in the protocol or SOP.

In the absence of the Field Coordinator, the ranking field group person has primary responsibility for safety while working in the field.

6.0 STUDY-SPECIFIC DECISIONS

Management, Project Supervisor and Project Leader are responsible for the following study-specific decisions:

6.1 Selection of study personnel
6.2 Responsibilities of each team member

7.0 REFERENCES

Goh, K.S. Responsibilities of Field Coordinator for EHAP studies. Memorandum to EHAP Personnel, dated 9/24/93.

Sanders, J. Responsibilities of Project Leaders Regarding Chemical Analysis. Memorandum to EHAP Staff, dated 6/13/88.

Sanders, J. Lab Liaison Personnel and Policy. Memorandum to EHAP Personnel, dated 7/1/87.

APPENDICES

Figure 1. Department of Pesticide Regulation Personnel Organization

Figure 2. EHAP Study Personnel Organization

Figure 1

Department of Pesticide Regulation Personnel Organization

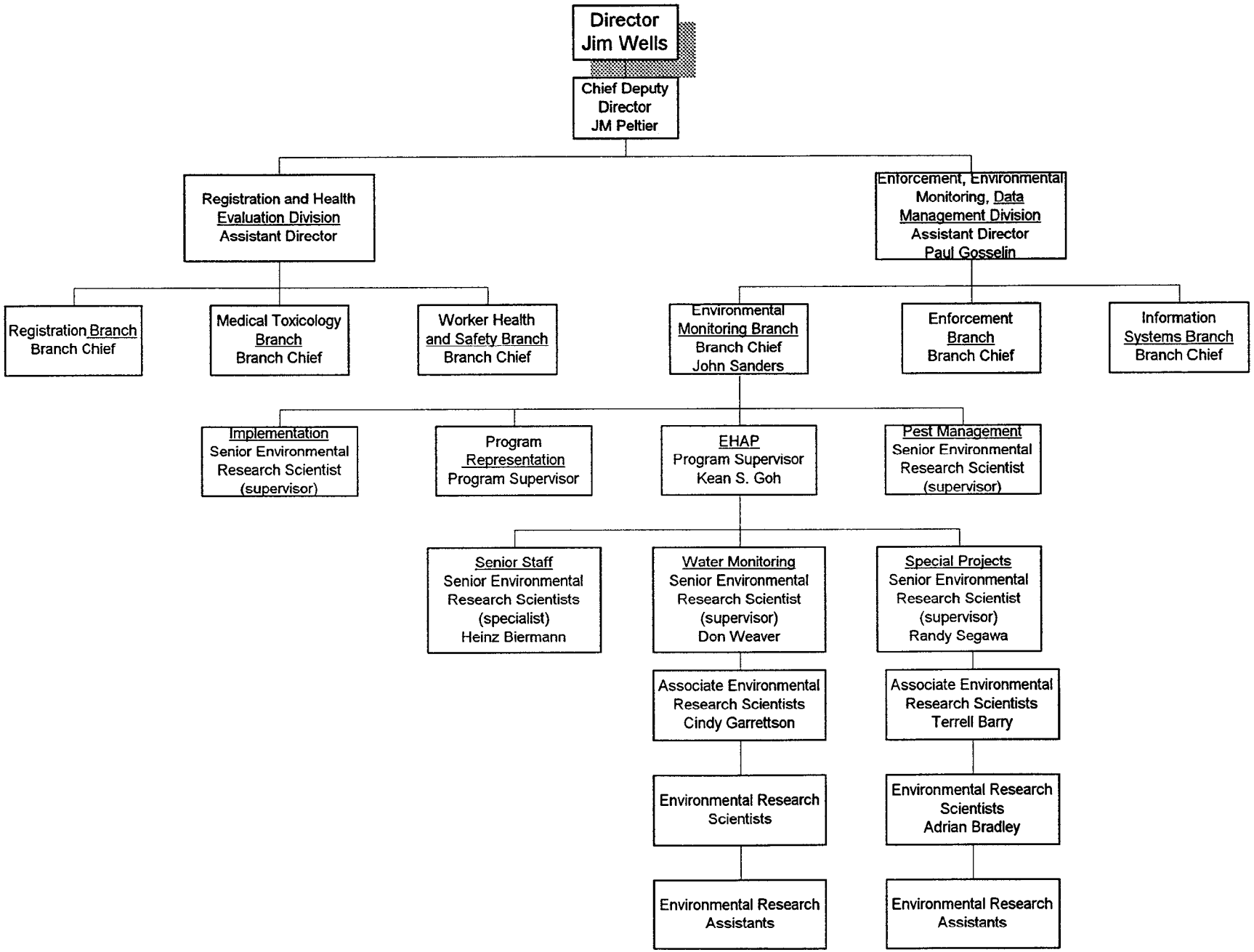
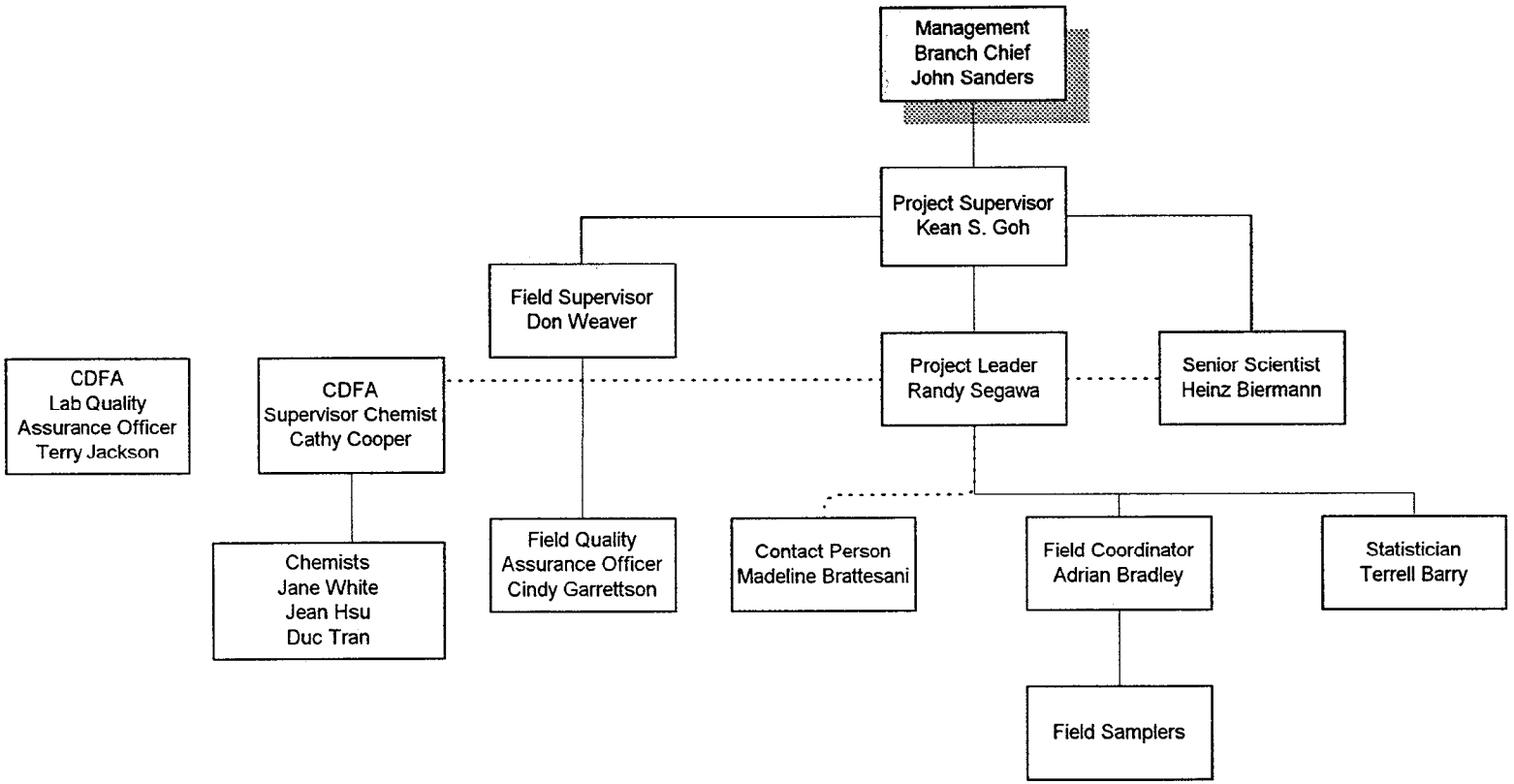


Figure 2

EHAP Study Personnel Organization*



*For GLP studies, the Senior Scientist and Quality Assurance Officer make up the Quality Assurance Unit and report to Management

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
830 K Street, Suite 200
Sacramento, California 95814

STANDARD OPERATING PROCEDURE

Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

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KEY WORDS-
Ice chest, sample, ice, temperature

APPROVALS

APPROVED BY: _____ DATE: 9/25/99
Kean S. Goh, Management

APPROVED BY: _____ DATE: 9/7/99
Lisa Ross, EHAP Senior Scientist

APPROVED BY: _____ DATE: 9/7/99
Carissa Ganapathy, EHAP Quality Assurance Officer

REVISED BY: _____ DATE: 9/2/99
DeeAn Jones, Environmental Research Scientist

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

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1.0 INTRODUCTION

1.1 Purpose

To ensure that samples are adequately packed in the field to avoid breakage and that samples are stored at the appropriate temperature for each media.

1.2 Scope

This document will provide specific instructions for packing and transporting samples after they have been collected. For instructions on how to package sampling materials prior to collection, see Standard Operating Procedure QAQC005.00.

2.0 MATERIALS

2.1 Ice chests
2.2 Wet ice or blue ice for cooling water or vegetation samples
2.3 Dry ice for cooling soil, air, or vegetation samples
2.4 Appropriate packing material for sample containers (ex: styrofoam 6-packs for quart jars and 1 L Amber bottles)
2.5 Hobo® Temp data logger or Min/Max Temperature recorder
2.6 Bubble plastic or other packaging material
2.7 Duct tape or packing tape
2.8 Permanent black marker
2.9 White label tape

3.0 PROCEDURES

3.1 SAMPLE TRANSPORT FROM THE FIELD TO THE WAREHOUSE OR LABORATORY

Before leaving the warehouse (sometime prior to sample collection), an ice chest should be filled with the appropriate ice (wet, dry, blue). This is to ensure that the samples are chilled immediately after collection. If the study is conducted under Good Laboratory Practices, a Hobo® Temp data logger or Min/Max Temperature recorder should be placed in each ice chest. Instructions for operating a Hobo® Temp data logger are found in Standard Operating Procedure EQOT001.01.

3.1.1 Place samples in styrofoam holders or other containers in ice chests immediately after sampling in the field or removal from storage refrigerators or freezers at an Environmental Hazards Assessment Program warehouse facility.

3.1.2 Surround the samples with sufficient ice to chill to the appropriate temperature. For **water samples** and **vegetation to be analyzed for internal and/or dislodgeable residue**, use wet ice or blue ice to chill the samples to 4°C. For **air**, **soil**, and **vegetation to be analyzed for total residue** use dry ice to chill the samples to -10°C to -70°C. It is preferable to maintain total pesticide residue samples at -70°C. If dry ice is not available, use any form of refrigeration in the following order of desirability: 1) freezer, 2) refrigerator, 3) blue ice, 4) wet ice (Sava, 1994). If the study is conducted under Good Laboratory Practices, the time and date the samples were placed in the ice chest should be recorded in the field notebook.

3.1.3 Check the samples often, making sure there is enough ice to maintain the required temperature. Add more ice when necessary, and drain off water as wet ice melts.

3.2 ADDITIONAL SHIPPING PROCEDURES

3.2.1 Pack samples securely by either adding packing material or wrapping containers in bubble plastic in order to prevent breakage.

3.2.2 Chain of custody (COC) records must accompany samples at all times and should be filled out according to Standard Operating Procedure ADMN006. Secure COCs in plastic bags and tape to the inside of the ice chest lid.

3.2.3 Using duct or packing tape, wrap the ice chest twice to seal the opening. This will alert the sample custodians to whether or not the ice chest has been tampered with.

3.2.4 If the ice chest is not already labeled, use the permanent marker and label tape to address the package to the appropriate destination. Note: Certain shipping companies may require a specific label to be used. Also, check with the airline or shipping company for any restrictions, including type of ice to be used.

3.3 RECEIVING

Samples that have been shipped to the West Sacramento warehouse, will be received by a sample custodian. This custodian will follow Standard Operating Procedure QAQC003.01 for check-in and check-out methods. Additionally, the custodian will notify the EHAP QA officer and project leader of any samples broken during transport and record the condition on the corresponding COC.

4.0 REFERENCES

Sava, R. 1994. Guide to Sampling Air, Water, Soil, and Vegetation for Chemical Analysis. Department of Pesticide Regulation - EHAP report EH 94-04. Sacramento, California.

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STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

KEY WORDS

Sample Tracking, Sample Tracking Database, Chain-of custody, Sample

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Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMIN002

STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) discusses sample check-in and check-out procedures; the recording of chemistry data; sample disposal procedures; and the Sample Tracking Database.

1.2 Definitions

1.2.1 **Sample** is any environmental substance collected and analyzed for chemical content, toxicity, soil texture analysis, etc.

1.2.2 **Sample Tracking Database** is a relational database designed in Microsoft Access to trace a sample from the time it is checked into the storage facility until the sample is submitted to a laboratory for analysis or disposed of after a study is completed.

1.2.3 **Chain-of-custody** is a record describing in detail all pertinent information specific to each sample, including dates and signatures of persons handling the sample.

1.2.4 **Sample Custodians** are personnel, under direction of the lab liaison, responsible for receiving samples from field staff, delivering samples to the laboratory, and tracking samples in the Sample Tracking Database.

2.0 SAMPLE TRACKING

2.1 Sample Tracking Codes

Sample tracking codes are abbreviations for fields in the database that refer to specific information about each sample. The study number in combination with the sample number is identified as the key field and all information specific to the sample is referenced by the following codes back to the key field.

STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

SAMPLE CODES:

P= Primary	R= Replicate	B= Backup	FB= Field Blank
* = Split	S= Spike	BG= Background	BM= Blank Matrix
A= Acidified	U= Unacidified	RB= Rinse Blank	

STORAGE LOCATION CODES refer to the storage location of each sample and the storage facility.

F= Fresno	R= Refrigerator	SR10= Sacramento Refrigerator #10
S= Sacramento	F= Freezer	SF05= Sacramento Freezer #05
W= Warehouse	A= Air Temp	SF06= Sacramento Freezer #06
L= Lab	I=Ice Chest	SF07= Sacramento freezer #07
D= Deep Freeze	FZ= Freezesafe	

SAMPLE TYPE CODES refer to the sample matrix collected.

FRU= Fruit	DVEG= Dislodgeable Vegetation	TWG= Twigs
SOI= Soil	SSS= Stainless Steel Sheets	EXT= Extract
WAT= Water	STD= Standard	VEG= Vegetation
SUR= Surrogate	SED= Sediment	FILT= Filtrate
TUR= Turf	TAN= Tank	KIM= Kimbie
SAN= Sand	AIR= Air	TRP= Air Cassettes
BRA= Branch		

SAMPLE CONTAINER CODES refer to the type of container each sample is placed in during storage.

QMSJ= Quart Mason Jar	1LAMBR= 1 Liter Amber Bottle
PMSJ= Pint Mason Jar	HPMSJR= Half Pint Mason Jar
PBAG= Plastic Bag	HIVJAR= Hi-Vol Jar
FOIL= Aluminum Sheets	P500mL= Plastic Bottle (500 mL)
CAS= Air Cassettes	1LPC= 1 Liter Polycarb. Bottle

1LPP= 1 Liter Polyprop. Container
XADT= XAD Tube (small)
Summa= Summa Canister
HIV= High Volume Air Sampler_
500mLPC= 500mL Polycarb. Container
250mLAMBR= 250mL Amber Bottle
500mLAMBR= 500mL Amber Bottle
500mLHDPP= 500mL High Density Polyprop.
VIAL= Small Standard Vial
XAD4= Large XAD 4 Tube
LOV= Low Volume Air Sampler

LABORATORY CODES refer to the specific laboratory each sample is shipped to for analysis.

QUAN= Quanterra Laboratory
ATL= Aquatic Toxicology Lab
FMC= FMC Corporation
ZEN= Zeneca Ag Products
APPL= Apple Labs
NCL= North Coast Labs
FRES= Fresno Soils Lab
CDFA= CA Dept. of Food & Agr.
CDFG= CA Dept. of Fish & Game
ALTA= ALTA Analytical Laboratory
VAL= Valent Dublin Laboratory
MOR= Mores Laboratories Inc.
UCD= University California Davis
WSAC= W. Sacramento Soils Lab

ANALYSIS TYPE refers to the type of test method to be performed on each sample.

C= Chemical
O= Organic
T= Texture
F= Tracer
P= pH
B= Bulk Density
E= Elisa
M= Moisture
V= Various

CHEMICAL ANALYSIS refers to the chemical analysis to be performed on each sample, if applicable.

OP=Organophosphate Screen
CB= Carbamate Screen
DI= Diazinon
EN/DI= Endosulfan/ Diazinon Screen
TOX= Biotoxicity
HEX=Hexazinone
TRI= Triclopyr
GLY= Glyphosate
TRIAZ= Triazine Screen

TDM= Triclopyr, 2,4-D, MCPA
PIC= Chloropicrin
MOL= Molinate
CARBO= Carbofuran
MeBr= Methyl Bromide
PROP= Propanil
THIO= Thiobencarb
MP/MN= Methyl Parathion/Malathion

COMMENTS refers to any additional information regarding samples.

BS= Blind Spike
ACT TOX= Acute Tox
CHN TOX= Chronic Tox
RB= Rinse Blank
GF= Golden Fleece
BB=Buck Brush
BF= Bracken Fern
MB= Manzanita Berry
SR= Soap Root
DB= Deer Brush
EB= Elderberry
DG= Deergrass
RD= Redbud
PE= Pearly Everlasting

2.2 Sample Check-in Procedures

All samples received at the storage facility are immediately put in a refrigerator or freezer depending on the matrix specific storage requirements. The field crew fills out a three part check-in sheet (Figure A) using the sample tracking codes (Section 2.1).

The check-in sheet must be complete in order to properly track environmental samples. The following is a description of each key component of the check-in sheet.

Portion Filled Out By Field Staff

Project ID: The study number or name.
Date Received: The date the sample was received from the field crew.
Checked-in by: The initials of the person who fills out the check-in sheet.
Remarks: List ice chest number where samples were stored, Hobo Temp® temperature logger number (if necessary), and any additional or necessary information regarding the samples listed on the check-in sheet. For GLP studies, the ice chest number along with the maximum temperature samples were stored at in the ice chest must be marked on Hobo Temp® print-out as noted in SOP EQOT001.01. If temperature exceeded 6° C for refrigerated samples or 0° C for frozen samples, this must be documented on the sample check-in sheet in the comments section.
EHAP Sample No.: The number assigned to a labeled sample container.
Sample Code: List sample code (Section 2.1 for codes).

Date Sample Collected: Note the sample collection date from the Chain-of-Custody.
Sample Type: Specify the type of sample collected (Section 2.1).
Container Type: What the sample is stored in (Section 2.1).
Analysis Type: The type of analysis the sample is intended for (Section 2.1).
Analysis: List the type of chemical or screen the sample is to be analyzed for.
Comment: Space provided for additional information regarding individual samples (Section 2.1).

Portion Filled Out By Sample Custodian

Date/Logged in by: The date and person who enters information into the Sample Tracking Database.
Storage Location: List where the sample is being stored (Section 2.1).

After the check-in sheet is completed, the white and yellow copy are used to enter the information into the Sample Tracking Database and then filed with the QA/QC officer. The pink copy is given to the project leader in order to track ice chests and corresponding samples entering the storage facility (GLP studies only).

Each field sample is compared against it's corresponding Chain-of-custody (COC), then the COC is signed and dated by the person receiving the sample at the storage facility. The white and yellow copy of each COC is removed and sent with it's corresponding field sample to the laboratory. The pink COC copy is given to the Project Leader. Any remaining samples held at the storage facility are stored under their required storage conditions with the white and yellow copy of their corresponding COC's.

2.3 Sample Check-out Procedures

A three part check-out sheet is filled out for any sample leaving the storage facility (Figure B). The check-out sheet must be complete in order to properly track environmental samples leaving the storage facility. The check-out sheet is filled out by the sample custodian only.

The check-out sheet is similar to the check-in sheet but differs in three components.

> **Date Delivered:** The date the sample is taken to the laboratory.
> **Checked-out by:** The initials of the person filling out and transporting the sample to the laboratory.
> **Laboratory Delivering to:** Specify the destination code for the sample scheduled for analysis (Section 2.1).

A pink copy of the check-out sheet and the white and yellow copies of each COC are placed in a plastic bag and accompany samples transported to the laboratory. The samples are placed in ice chests and maintained at their required temperatures during transport using blue ice, wet ice or dry ice. The white and yellow copies of the check-out sheet are retained by the QA/QC officer and are used to enter information into the Sample Tracking Database.

2.4 Chemistry Results

After results are received from the laboratory, the laboratory sample number, and the extraction and analysis date for each sample are entered into the Sample Tracking Database using the appropriate Microsoft Access query.

2.5 Sample Disposal

After each study is completed, and with the approval of the Project Leader, all remaining samples stored in the storage facility may be disposed of by the sample custodian. A two part Sample Disposal Sheet is completed and includes information similar to the check-out sheet (Figure C). This information is then entered into the Sample Tracking Database using the appropriate Microsoft Access query. The white copy of the Sample Disposal Sheet is retained by the QA/QC officer while the yellow copy is used to enter the information into the database.

3.0 Sample Tracking Database

All the information reported on the check-in, check-out, and sample disposal sheets is entered in the Sample Tracking Database using tables in Microsoft Access. Queries, forms and reports are designed specifically for each study to access fields for summarizing data.

3.1 Computer Generated Backups

Weekly backups are conducted by copying the database to a zip drive disk.

FIGURE A

SAMPLE **CHECK-IN** SHEET ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

Study Number (Project ID):_____

Date Received (Warehouse):_____

Checked-In By:_____

Page ____ of ____

Sample Tracking Staff Only:

Logged In By (data entry):_____

Data Entry Date:_____

Storage Location Code:_____

Remarks:

Samples were stored in ice chest # _____ at check-in.

EHAP Sample #	Sample Code	Date Sample Collected	Sample Type	Container Type	Analysis Type	Analysis	Comments

(3/99) White copy-Lab Liaison, Yellow-Sample Tracking Staff, Pink-Project leader

FIGURE B

STATE OF CALIFORNIA

DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
West Sacramento Field Office
3971 Commerce Drive, Suite D
West Sacramento, CA 95691 (916) 322-3082

SAMPLE **CHECK-OUT** SHEET

Study Number (Project ID):_____ Logged Out By (data entry):_____

Date Delivered:_____ Data Entry Date:_____

Checked-Out By:_____ Storage Location Code:_____

Laboratory Delivering To:_____ Page ____ of ____

Remarks:

EHAP Sample #	Sample Code	Date Sample Collected	Sample Type	Container Type	Analysis Type	Analysis	Comments

(5/98)

White copy-Lab Liaison, Yellow-Sample Tracking Staff, Pink-Laboratory

FIGURE C

California Dept. of Pesticide Regulation
Environmental Hazards Assessment Program
3971 Commerce Drive, Suite D
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Today's Date:_____

Sample Disposal Sheet

Project ID (Study no.): _____ Disposed by: _____

Date Disposed: _____ Storage location: _____

==========

Remarks:

==========

EHAP Sample #	Sample Code	EHAP Sample #	Sample Code	EHAP Sample #	Sample Code	EHAP Sample #	Sample Code

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STANDARD OPERATING PROCEDURE
Equal-Width-Increment Sampling of Surface Waters

KEY WORDS-
Increment; flow; discharge; cross section; transit; vertical

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Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Equal-Width-Increment Sampling of Surface Waters

1.0 INTRODUCTION

1.1 Purpose

This Standard Operation Procedure (SOP) discusses the specific procedure for sampling surface water using the equal-width-increment (EWI) method. A cross-sectional flow-integrated sample obtained by the EWI method will produce a water sample volume that is proportional to the amount of flow at each of several, equally spaced, predetermined verticals in the stream cross section. This document gives instruction on A) determining the number of verticals, B) determining a transit rate, and C) collection of a sample volume.

1.2 Definitions

In the context of this SOP, surface water is defined as all inland waters, excluding groundwater.

2.0 MATERIALS

2.1 Wading rod
2.2 D-77 Sampling Unit- bronze or aluminum
2.3 Bridge Board/Crane and Reel
2.4 5/16" Nozzle/Cap Assembly
2.5 3-liter Teflon® Bottle
2.6 Tag-line or Tape Measurer
2.7 Composite Sample Container (such as stainless steel milk can)
2.8 Stopwatch
2.9 Waders (for wading rod method)

3.0 PROCEDURES

Instructions included here are modified from the following document: Edwards, T.K. and D.G. Glysson (1988).

3.1 Determine the Number of Vertical Cross-sections for Sampling

3.1.1 Looking downstream from the sampling site, measure the horizontal distance from the left edge of water to the right edge of water.

3.1.2 Visually inspect the stream from bank to bank, observing the water velocity and depth distribution as well as apparent distribution of sediment in the cross sectional area.

3.1.3 Determine the horizontal width of the increment that represents approximately 10% of the flow at that part of the cross section where the "unit width discharge" is highest (generally the deepest, fastest section). To determine stream discharge, see USGS manual, “Discharge Measurements at Gaging Stations”, Book 3, Chapter A8. **This increment must be used for the entire cross section.** Typically, this works out to be from 10 to 20 equal increments for streams 5 or more feet wide. For example, if the stream width determined from the tag-line or tape measure is 160 feet wide and the cross-section where the highest unit width discharge was determined to be 10 feet, then the number of verticals required is 16. The sampling station within each width increment is located at the center of the increment. In this example, the first sampling station would be at 5 feet from the river bank’s edge. The subsequent 15 verticals are then spaced 10 feet apart, resulting in sampling stations at 15, 25, 35, 45, ... and 155 feet. For fairly even flowing and level bottomed streams, only 10 verticals may be needed.

3.1.4 If the stream is < 5 feet wide, divide into as many equal increments as possible, with the minimum increment width being 3 inches.

3.2 Transit Rate

3.2.1 Using the data collected when gauging discharge, identify the fastest flowing increment in feet per second (fps) in the stream cross section. This velocity rating will determine which sampling device to use. Generally, the bronze D-77 operates at velocities up to 7.2 feet per second, and the aluminum D-77 to 3.3 feet per second. A wading rod should be used at slower moving, shallow sampling sites, where wading is safe.

3.2.2 Begin at the vertical determined from step 3.2.1 and lower the sampling unit (D-77 or wading rod) until the 3-liter Teflon® bottle’s nozzle is just above the surface of the stream.

3.2.3 Using a stopwatch, determine the amount of time (in seconds) and number of transits (up and down movements of sampling unit through the water column at a slow, steady rate) that it takes to fill the sampling bottle without overfilling. (A bottle is overfilled when the water surface in the bottle is above the nozzle or air exhaust

with the sampler held level.) The bottle does not fill on downward movements, only when it is being raised. However, it is important to maintain a steady rate in both directions in order to remain consistent and to minimize stream disturbance. Several iterations will be required to determine the final transit rate based on the amount of water to be collected. **This transit rate must be used at each vertical (sampling station)**. It is possible to sample at two or more verticals using the same bottle if the bottle is not overfilled.

3.3 Sample Collection

3.3.1 Begin sampling at first vertical station determined in step 3.1.3 and lower the sampling unit until the bottle's nozzle is just above the water surface.

3.3.2 Using the transit rate determined in step 3.2.3, lower unit into stream and raise to just below the surface once bottom is felt. The movement of the sampling unit throughout the water column must be constant and with minimal disturbance of the stream bottom. Continue across stream, collecting water at each vertical (sampling station), depositing collected water into a composite sample container. Complete the necessary number of transects, until desired volume is obtained. **Note: An equal number of transits must be made at each vertical.**

4.0 STUDY-SPECIFIC DECISIONS

Study specific information should be included in the study protocol, a separate document describing a specific study.

5.0 REFERENCES

Edwards, T.K. and D.G. Glysson. 1988. Field Methods for Measurement of Fluvial Sediment**,** U.S. Geological Survey Open-File Report 86-531. pp. 61-64.

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STANDARD OPERATING PROCEDURE

Instructions for Splitting Water and Rinsing the Geotech® Dekaport Splitter and Splitting Equipment

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KEY WORDS-
Splitter; rinse; cross-contamination

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Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE

Instructions for Splitting Water and Rinsing the Geotech® Dekaport Splitter and Splitting Equipment

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1 .O INTRODUCTION

1.1 Purpose

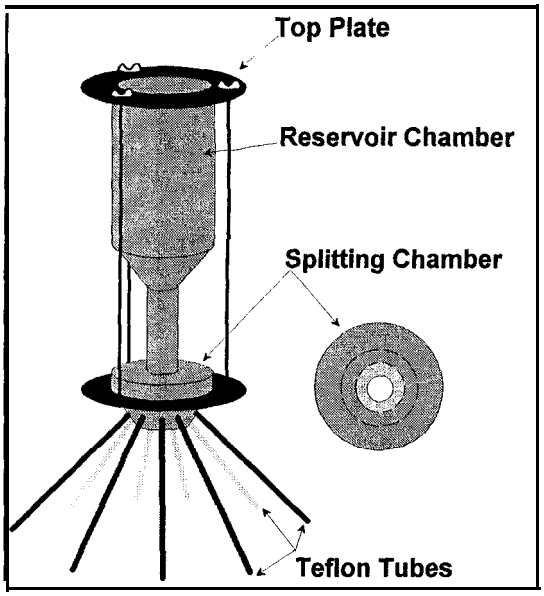
To ensure effective mixing and splitting of a surface water sample when various paired analyses are to be performed and to describe proper cleaning of equipment to prevent cross-contamination.

1.2 Scope

This document will provide specific instructions for splitting surface water samples and rinsing the splitter.

2.0 MATERIALS

2.1 Large glass jars, stainless steel milk can or container large enough to hold sample water that will be split
2.2 Water sample
2.3 Geotech® 10 port splitter
2.4 Sample containers
2.5 Stainless steel buckets, funnel
2.6 Chain of Custody records
2.7 Latex gloves
2.8 Deionized water (3 or more gallons)
2.9 Leveler
2.10Large Plastic Bags



3.0 PROCEDURES

Samples should be transported in a glass or stainless steel container on wet ice (4°C), from collection site to the site where splitting will occur.

3.1 Splitting Procedure

3.1.1 Place the pre-cleaned (see EQWA001) Geotech® dekaport water splitter on level ground. Make sure all splitter water spouts are level to ensure

a fairly even water flow. Place a level across the top of the splitter to ensure that it is level.

3.1.2 Set up to a maximum of 10 sample containers under each Teflon port. If exactly 10 l-liter sample containers (or smaller) are required, use one port per container. If less than 10 samples are required, use fewer ports, or two tubes can be placed in each container. However, all bottles must be treated the same way each time a sample of water is to be split so that each sample contains the same amount of water and sediment. When there are more than ten sample bottles, e.g. 15, then divide the splitter spouts between two buckets and pour the water through the splitter. Then pour the water from one bucket through the splitter into half the sample bottles, then pour the water from the other bucket through the splitter into the remaining bottles. Collect excess water from unused spouts in an uncontaminated bucket or preferably a container used to hold the water sample originally (e.g., a Teflon sampling bottle). This water can be poured through the splitter again to fill the bottles completely.

3.1.3 Immediately before pouring collected sample water into the splitter, mix water inside a glass or stainless steel sample collection container to suspend the sediment. If more than one container was used to collect the sample, mix the separate containers together in a larger container such as a stainless steel milk can. Prior to completely pouring the remainder of the sample water out of the sample containers into the milk can, or into the splitter directly, swirl the water one last time to ensure that all the remaining sediment stays with the sample water and not at the bottom or along the sides of the container.

3.1.4 While pouring the sample water through the splitter, keep the water level near the top of the reservoir chamber so that as much head pressure is maintained as possible to ensure even flow through the spouts. Again, prior to pouring out the last of the sample water, swirl to get the sediment suspended.

3.1.5 Cap all sample containers and rinse the splitting equipment as described below.

STANDARD OPERATING PROCEDURE
Instructions for Splitting Water and Rinsing the Geotech® Dekaport Splitter and Splitting Equipment

3.2 Rinsing Procedure

3.2.1 If the splitting is conducted at a facility, rather than out in the field, rinse the splitter and all equipment thoroughly with tap water, then proceed to the next step. If splitting is conducted in the field, rinse the splitter and all equipment with deionized-distilled water and add one rinse (see 3.2.3 below).

3.2.2 Rinse the splitter and associated equipment after splitting any water sample by pouring approximately 2 L of deionized water into either the milk can or steel bucket used in the splitting procedure. Then swirl the water to wash out residues. Pour that same water into the next piece of equipment (such as another bucket that was used for splitting), and again swirl the water and pour into another piece of equipment. This continues through all the equipment and ends by pouring the deionized water through the splitter.

3.2.3 This process is completely repeated from start to finish three times, each time with new, uncontaminated 2L volume of deionized water. If initial rinse did not include tap water, as in 3.2.1, then rinse with deionized water once more.

3.2.4 Cover all containers and the splitter with clean plastic bags between uses.

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STANDARD OPERATING PROCEDURE

Instructions for using the Hobo®Temp Temperature Data Logger

KEY WORDS-
Temperature, data logger, Hobo®Temp

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PREPARED BY: Carissa Ganapathy DATE: 6/1/99
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Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Instructions for using the Hobo®Temp Temperature Data Logger

1.0 INTRODUCTION

1.1 Purpose

A temperature recording device such as a Hobo®Temp data logger should be placed in ice chests carrying samples from the field to the warehouse to verify that proper temperature was maintained during transport. Data recorded by the data logger can then be downloaded to a personal computer (PC), examined, and stored with other information collected. This procedure must be followed for all studies requiring Good Laboratory Practices (GLP).

1.2 Scope

This document will provide specific instructions for recording temperature and downloading data to a PC using a Hobo®Temp data logger. This SOP will also describe the procedure for documenting sample temperatures out of range.

2.0 MATERIALS

2.1 Hobo®Temp data logger.
2.2 Computer, Boxcar® software, interface cable
2.3 Ice chest
2.4 Wet ice or dry ice
2.5 Small plastic bag
2.6 Tape
2.7 Check-in sheet
2.8 Chain of Custody (COC)
2.9 Mason Jar with lid

3.0 PROCEDURES

3.1 Launching the Hobo®Temp data logger

3.1.1 Connect the interface cable to the computer serial comm port. Then connect the other end of the cable to the jack on the data logger.

3.1.2 Click on the BoxCar® application in the sample tracking menu on the PC. Then click on logger on the tool bar and select launch.

3.1.3 Enter a study description for a file name, which could include a study number, a date or alphanumeric code. For example: for study 159, enter today's date (25feb98a) with an a, b, or c representing the forest to be sampled.

There is no need to add an extention since at this point the default extension will be .dtf. Next, select the time interval to be used between temperature readings. Five to six minutes should be adequate. Click on the advanced options, then remove the X in the wrap selection (to keep data from being overwritten), if it is present. Now click start.

3.1.4 When it is ready for use, the light on the logger will blink faintly.

3.2 Recording data in the field

Place the logger in the ice chest when leaving the West Sacramento warehouse. Keep the logger dry. When using dry ice, place the logger in a plastic bag and tape it to the inside top of the Freeze-safe or ice chest lid. When using wet ice, place the logger in a mason jar, close the lid, then place the jar along side of the samples, under the ice. If the logger becomes wet, open it, remove the battery and let the logger dry.

3.3 Note taking and record keeping

3.3.1 Note the identification number for the ice chest used to transport samples in the field notebook. If more than one logger is used during a sampling trip, mark each logger with the ice chest number so that they do not get mixed up when they are removed from the ice chest.

3.3.2 Also record the ice chest number on the check-in sheet, remarks section, so that each sample can be matched to an ice chest and transit temperature. If several ice chests were used, indicate which samples were transported in each ice chest. The pink portion of the check-in will be given to the project leader and the ice chest number will be recorded in the sample tracking database for each individual sample.

3.4 Reading data from the Hobo®Temp data logger

3.4.1 Reconnect the logger with the cable to the computer serial comm port.

3.4.2 Click on the BoxCar® application, then click on logger on the tool bar and select readout. The logger will now download the data into the computer.

3.4.3 After the data is downloaded, the data will be plotted and save as will appear. Save the file under the same file name given when launched. However, the default extension may be changed to a description as well. Example: for study number 159, save the data in the C:\boxcar 3\ forest directory as the description already entered when launched, but add the extension .159 to the end (e.g., 25feb98a.159). Click okay.

3.4.4 Print a copy in landscape, not portrait mode. By drawing arrows or somehow marking the plot, note the time samples were added and removed from the ice chest. Note temperatures exceeding maximums as in 3.5, then write the ice chest number on the printout.

3.5 Recording out-of-range sample temperatures

Examine the plotted temperature recording. If the recorded maximum temperature after initial cooling in the ice chest exceeded 5°C for samples on wet ice or 0°C for samples that were to be frozen, mark the maximum temperature on the check-in sheet in the remarks section and the COCs for each sample stored in that ice chest. Also check the ice chest for cracks or damage that could cause the temperature to exceed maximums. Give the plotted temperature printout to the project leader.

California Department of Pesticide Regulation
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830 K Street
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STANDARD OPERATING PROCEDURE

Instructions for Preserving Water Samples Using Hydrochloric Acid (HCL)

KEYWORDS-
Acidification, calibration, preservation, pH

APPROVALS

APPROVED BY: _____ DATE: 10/13/98
Management

APPROVED BY: _____ DATE: 10/5/98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 10/1/98
EHAP Quality Assufance Officer

PREPARED BY: Adrian Bradley / Carissa Ganapathv DATE: 10/1/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Instructions for Preserving Water Samples Using Hydrochloric Acid (HCL)

1 .O INTRODUCTION

1 .I Purpose

The stability of pesticides in water varies greatly. Preserving water samples may slow the degradation of some pesticides. The decision to preserve a sample and the preservation method should be chosen based on a storage stability study (SOP QAQCOOI) and in consultation with the chemists, project leader and lab liaison. One routinely used procedure is to add 3 N hydrochloric acid (HCL).

1.2 Scope

This document will provide specific instructions for preserving water samples by acidification with HCL.

2.0 MATERIALS

2.1 Portable pH meter (accurate to a least 0.1)
2.2 pH equipment listed in SOP EQWA002
2.3 Clean 1,000 ml beaker
2.4 Deionized (DI) water in a squirt bottle
2.5 3 N HCL in dropper bottle
2.6 Disposable gloves
2.7 Water Quality Sheet and Chain of Custody (COC)

3.0 PROCEDURES

3.1 Sample Preservation

Refer to the study protocol to determine the method of preservation as well as the replicates needing acidification. Below is a list of analytes and screens commonly sampled by this branch that may require acidification and a list of chemicals that should not be acidified. Remember this is a general guide, and when they differ, the study protocol should be followed.

STANDARD OPERATING PROCEDURE
Instructions for Preserving Water Samples Using Hydrochloric Acid (HCL)

Screen or Analvte	**Acidification**
Organophosphate (OP) screen: Chlorpyrifos, azinphos-methyl, DDVP, ethoprop, phosalone, thimet, dimethoate, fonofos, malathion, methidathion, methyl parathion and Phosmet	Yes
Diazinon (DI): *note* this OP breaks down rapidly when acidified	No
Carbamate (CB) screen: carbaryl, carbofuran, aldicarb, methiocarb, methomyl, and oxamyl.	Yes
Phenoxv (PH) screen: 2,4,-D, MCPA, and Triclopyr	No
Glvphosate (GL)	No
Triazine (TR) screen: Atrazine, bromacil, diuron, Cyanazine, hexazinone, metribuzin, prometon, prometryn and simazine. Sometimes norflurazon and some breakdown products included.	No
Molinate (ME)	No
Thiobencarb (TB)	No
Endosulfan isomer and breakdown product	No

Sometimes the following are requested: (see protocol)

(BA) Back-up Acidified sample (back-up for acidified samples)	Yes
(BU) Back-up Unacidified sample (back-up for samples not acidified)	No

3.2 pH Determination and acidification

3.2.1 pH determination for preservation should be performed using sample water and the same volume of water contained in the sample bottles. For instance, for a l-Liter Amber bottle, **fill a 1,000 ml beaker to the 1,000 ml level with the sample water. For ground water** sampling, fill a beaker with water while the pump is operating.

STANDARD OPERATING PROCEDURE
Instructions for Preserving Water Samples Using Hydrochloric Acid (HCL)

3.2.2 Determine pH of the sample water in the beaker by following SOP EQWA002.

3.2.3 Using a dropper, slowly add 3 N HCI to the water while gently stirring with a clean glass rod or the pH meter probe. For pH meters without an attached probe (one-unit) do not wet the pH meter above the immersion line (indentation on plastic) as this will wet the electronic portion of the meter which could affect the accuracy of the instrument. Add drops until the pH reaches between 3.0 to 3.5.

3.2.4 The final pH and number of HCI drops used should be recorded on the water quality sheet and on the COC matching each sample bottle that needs to be acidified.

3.2.5 Add the determined number of drops to the samples requiring acid preservation. Be careful not to over fill the bottle because the acid may pour off the side and the sample may not be properly preserved.

3.2.6 Cap all bottles and cool to 4°C using wet ice, blue ice or place in a refrigerator.

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STANDARD OPERATING PROCEDURE
Instructions for Rinsing Surface Water Sampling Containers

KEYWORDS-
Rinse; cross-contamination; cleaning

APPROVALS

APPROVED BY: _____ DATE: 10/13 98
Management

APPROVED BY: _____ DATE: 10/5/98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 10/11/98
EHAP Quality Assurance Officer

PREPARED BY: Cindy Garretson/Carissa Ganapathy DATE: 9/30/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Instructions for Rinsing Surface Water Sampling Containers

1 .O INTRODUCTION

1 .I Purpose

To ensure effective cleaning of surface water collection containers to prevent cross-contamination.

1.2 Scope

This document will provide specific instructions for rinsing surface water collection containers in the field. Rinsing may be conducted in the field when the containers are used at more than one site per day.

1.3 Definitions

1.3.1 Native rinse refers to collecting water from the same source as the intended sample prior to sampling, for use as a rinse of the collection containers. The purpose is to further remove trace residues of any constituent in the containers including drops of deionized water.

2.0 MATERIALS

2.1 Surface water collection containers (e.g. Teflon@ bottle, Teflon@ spout, Stainless steel buckets, funnel, stainless steel milkcan)
2.2 Latex, disposable gloves
2.3 Deionized (DI) water (10 or more liters)
2.4 Large Plastic Bags

3.0 PROCEDURES

3.1 Place one or two plastic bags on the ground to provide a clean working location.

3.2 While wearing disposable gloves, rinse the surface water collection containers that will be used at more than one site by pouring a minimum of 2 L of deionized water into one of the containers used. For example, pour 2L of deionized water into the Teflon' bottle. **Then swirl the water to wash out residues. Next put the Teflon@ spout on the** bottle and shake to clean residues off the inside of the spout, then pour that water through the spout into the next piece of equipment (such as a bucket), and again swirl

the water and pour into another piece of equipment. This continues through all the equipment and ends by discarding the water on the ground.

3.3 This process is completely repeated from start to finish three times, each time with new, uncontaminated deionized water, using a minimum of 2L with each rinse.

3.4 Cover all containers with clean plastic bags immediately after rinsing.

3.5 Do a native rinse prior to collecting the next sample using a similar volume of water as that collected for the sample.

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STANDARD OPERATING PROCEDURE
Procedure for Generating Rinse Blanks

KEY WORDS-
Rinse; decontamination; splitter

APPROVALS

APPROVED BY: _____ DATE: 6/25/98
Management

APPROVED BY: _____ DATE: 6/24/98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 6/23/98
EHAP Quality Assurance Officer

PREPARED BY: _____ DATE: 6/23/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Procedure for Generating Rinse Blanks

1 .O INTRODUCTION

1 .1 Purpose

Rinse blanks are created to assess the efficacy of equipment decontamination procedures described in SOPs FSWA004 and FSWA005.

1.2 Scope

This document will provide specific instructions for collecting rinse blanks from surface water sampling equipment and/or the water splitting equipment.

2.0 MATERIALS

2.1 Deionized water (sufficient to fill sample bottles)
2.2 Sample bottles (same number used for surface water analysis)
2.3 Clean Geotech® Dekaport port splitter
2.4 All containers used to collect or contain samples: e.g. Teflon® bottle, Teflon® spout, stainless steel buckets, milkcan, funnels
2.5 Chain of Custody records
2.6 Latex disposible gloves
2.7 Level

3.0 PROCEDURES

Rinse Blanks should be performed at least once every study or after each sample that represents 10% of the total number of samples collected in the study, whichever is more. Enough rinse blanks should be generated to analyze all chemicals analyzed for in **a** particular study. Rinse blanks should be collected from both sampling and splitting equipment, or both combined if all the equipment is cleaned and split at one location. Below is an example describing the procedure used for generating rinse blanks when both sampling and splitting equipment are used at one location.

3.1 Instructions for Generating Rinse Blanks

3.1.1 After the samples have been collected at the sampling site and the equipment listed in 2.3 and 2.4 above have been completely decontaminated according to SOP#s FSWAO04 and FSWAO05, the rinse blank may be collected.

3.1.2 Place the cleaned Geotech® Dekaport water splitter on level ground. Make sure all splitter water spouts are level to ensure a fairly even water flow. Place a level across the top of the splitter to ensure that it is level.

3.1.3 While wearing disposable gloves, set up the same number of sample bottles as used for surface water analysis, following instructions for splitting procedures in FSWAO04.

3.1.4 Pour about 500ml more deionized water than required to fill the rinse blank sample bottles into the first piece of sampling equipment (e.g. Teflon@ bottle). Swirl the water around and then pour the water into the next piece of sampling equipment (e.g. the milkcan).

3.1.5 Continue to pour the water and swirl until the water has rinsed all the sampling equipment. Prior to completely pouring the remainder of the sample water out of the sampling containers swirl the water one last time to ensure that any residual sediment stays with the sample water and not at the bottom or along the sides of the container. Lastly, pour the deionized water through the Dekaport splitter and fill the rinse blank sample bottles. If there are extra splitter spouts, put a clean bucket under the spouts. Pour the water from this bucket back through the splitter. Continue the process until all the bottles are full.

3.1.6 Cap all bottles and prepare COCs in the same manner as surface water samples. Add the words “Rinse Blank” to the comments section of the Check-In Sheet. If samples need to be acidified, add three drops of 3N HCL. Store samples at 4°C.

3.1.7 Cover all containers and the splitter with clean plastic bags.

APPENDIX II
Analytical Method Validation

Appendix II. Method Validation

Table 1. Method Validation Data (% recoveries) for Triazines, Bromacil and Diuron in surface water

Analyte	Spike Level	Recovery (% of spike)										
	ug/L	Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
Atrazine	0.1	99.0	98.0	103.0	96.0	96.0	98.4	2.88				
	0.5	80.0	91.6	94.4	101.0	95.2	92.4	7.75				
	2.0	108.0	93.0	107.0	94.5	98.8	100.3	6.95				
	6.0	106.0	107.0	107.0	107.0	108.0	107.0	0.71				
Overall:							99.5	7.28	121.4	114.1	85.0	77.7
Simazine	0.1	108	98.0	99.0	99.0	125.0	105.8	11.48				
	0.5	89.4	93.6	101.0	106.0	97.4	97.5	6.43				
	2.0	94.1	92.3	106.0	103.0	101.0	99.3	5.86				
	6.0	105.0	100.0	111.0	107.0	106.0	105.8	3.96				
Overall:							102.1	7.87	125.7	117.8	86.4	78.5
Diuron	0.1	90.0	102.0	102.0	71.0	82.0	89.4	13.33				
	0.5	83.6	84.4	90.2	93.2	95.8	89.4	5.35				
	2.0	84.7	86.6	102.0	84.5	95.5	90.7	7.78				
	6.0	95.2	90.3	104.0	93.6	98.9	96.4	5.26				
Overall:							91.5	8.41	116.7	108.3	74.6	66.2
Prometon	0.1	96.0	85.0	89.0	95.0	83.0	89.6	5.81				
	0.5	92.8	83.0	92.8	85.6	81.8	87.2	5.29				
	2.0	97.5	91.0	108.0	88.3	84.2	93.8	9.29				
	6.0	93.4	82.6	98.2	85.2	82.6	88.4	7.05				
Overall:							89.8	6.94	110.6	103.6	75.9	68.9
Prometryn	0.1	104.0	91.0	99.0	86.0	86.0	93.2	8.04				
	0.5	98.4	88.2	102.0	87.2	86.6	92.5	7.18				
	2.0	99.6	96.1	106.0	90.4	83.3	95.1	8.68				
	6.0	100.0	88.9	103.0	89.2	87.1	93.6	7.30				
Overall:							93.6	7.25	115.3	108.1	79.1	71.9
Bromacil	0.1	99.0	98.0	87.0	94.0	89.0	93.4	5.32				
	0.5	91.6	95.0	101.0	93.2	99.6	96.1	4.07				
	2.0	93.1	93.4	104.0	99.6	107.0	99.4	6.22				
	6.0	101.0	97.5	107.0	104.0	99.5	102	3.75				
Overall:							97.7	5.59	114.5	108.9	86.5	80.9
Hexazinone	0.3	99.3	99.7	99.3	102.0	122.0	104.5	9.87				
	0.5	85.6	90.6	105.0	88.8	107.0	95.4	9.87				
	2.0	96.4	97.6	101.0	103.0	105.0	100.6	3.60				
	6.0	99.7	92.2	99.7	98.3	104.0	98.8	4.26				
Overall:							99.8	7.67	122.8	115.1	84.5	76.8
Cyanazine	0.3	110.0	97.8	93.0	98.3	98.3	99.5	6.29				
	0.5	89.0	95.0	91.0	93.4	93.0	92.3	2.32				
	2.0	110.0	107.0	103.0	106.0	103.0	105.8	2.95				
	6.0	101.0	105.0	109.0	106.0	105.0	105.2	2.86				
Overall:							100.7	6.65	120.6	114.0	87.4	80.7

Appendix II. Method Validation

Table 1. Method Validation Data (% recoveries) for Triazines, Bromacil and Diuron in surface water

Analyte	Spike Level	Recovery (% of spike)										
	ug/L	Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
Metribuzin	0.3	98.7	96.3	95.7	86.3	90.3	93.5	5.04				
	0.5	86.8	91.6	92.4	87.6	90.4	89.8	2.46				
	2.0	93.2	93.0	91.4	96.9	88.9	92.7	2.92				
	6.0	90.0	97.7	97.3	89.3	99.7	94.8	4.79				
Overall:							92.7	4.11	105.0	100.9	84.5	80.4

1. SD = standard deviation
2. UCL = upper control limit. LCL = lower control limit. Upper and lower control limits = mean ± 3SD
3. UWL = upper warning limit. LWL = lower warning limit. Upper and lower warning limits = mean ± 2SD

Appendix II. Method Validation

Table 2. Method Validation Data (% recoveries) for Phenoxys in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
MCPA	0.1	81.0	91.0	85.0	96.0	78.0	86.2	7.33				
	0.5	96.0	97.8	96.6	101.0	104.0	99.1	3.36				
	2.0	104.0	106.0	115.0	91.0	112.0	105.6	9.29				
	10.0	107.0	82.5	91.9	87.8	92.9	92.4	9.12				
Overall:							95.8	10.23	126.5	116.3	75.4	65.1
2,4-D	0.1	96.0	95.0	96.0	71.0	116.0	94.8	15.96				
	0.5	83.4	85.0	95.8	89.0	99.6	90.6	6.96				
	2.0	97.0	98.0	114.0	87.0	105.0	100.2	10.03				
	10.0	96.1	70.1	80.9	80.5	84.1	82.3	9.32				
Overall:							92.0	12.17	128.5	116.3	67.6	55.5
Triclopyr	0.1	112.0	118.0	115.0	88.0	126.0	111.8	14.29				
	0.5	102.0	109.0	119.0	115.0	109.0	110.8	6.50				
	2.0	109.0	122.0	131.0	101.0	119.0	116.4	11.65				
	10.0	109.0	83.3	94.8	95.0	95.9	95.6	9.11				
Overall:							108.7	12.74	146.9	134.1	83.2	70.4

1. SD = standard deviation
2. UCL = upper control limit. LCL = lower control limit. Upper and lower control limits = mean ± 3SD
3. UWL = upper warning limit. LWL = lower warning limit. Upper and lower warning limits = mean ± 2SD

Appendix II. Method Validation

Table 3. Method Validation Data (% recoveries) for Glyphosate in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
Glyphosate	4.0	58.8	74.0	59.3	68.0	65.0					
	20.0	74.9	72.0	74.0	81.0	75.5					
	100.0	81.7	70.1	78.4	74.1	76.1					
Overall:						72.2	7.33	94.2	86.9	57.5	50.2

1. SD = standard deviation
2. UCL = upper control limit. LCL = lower control limit. Upper and lower control limits = mean ± 3SD
3. UWL = upper warning limit. LWL = lower warning limit. Upper and lower warning limits = mean ± 2SD

Appendix II. Method Validation

Table 4. Method Validation Data (% recoveries) for Organophosphates in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
DDVP	0.1	80.0	98.8	93.8	91.3	88.8	90.5	6.94				
	0.2	82.0	99.0	88.5	89.5	92.5	90.3	6.19				
	0.5	87.4	100.0	84.4	81.8	71.2	85.0	10.39				
	1.0	81.7	87.9	78.3	81.1	85.7	82.9	3.83				
	5.0	91.4	100.2	81.4	78.2	87.0	87.6	8.67				
Overall:							87.3	7.52	109.8	102.3	72.2	64.7
Dimethoate	0.1	106.3	100.0	100.0	98.8	103.8	101.8	3.14				
	0.2	100.5	84.5	102.5	94.0	108.5	98.0	9.15				
	0.5	105.4	108.8	95.4	103.4	100.2	102.6	5.11				
	1.0	91.8	109.0	85.1	102.0	97.4	97.1	9.19				
	5.0	97.6	104.4	92.8	89.8	96.6	96.2	5.52				
Overall:							99.1	6.78	119.5	112.7	85.6	78.8
Diazinon	0.1	90.0	100.0	97.5	101.3	88.8	95.5	5.77				
	0.2	82.0	99.0	93.5	77.0	90.5	88.4	8.86				
	0.5	91.8	97.4	89.4	89.4	85.4	90.7	4.40				
	1.0	83.0	93.7	82.4	84.7	85.9	85.9	4.55				
	5.0	93.8	93.6	88.2	83.6	89.0	89.6	4.24				
Overall:							90.0	6.22	108.7	102.5	77.6	71.4
M. Parathion	0.1	106.3	105.0	98.8	82.5	96.3	97.8	9.50				
	0.2	104.5	105.5	101.5	85.5	106.0	100.6	8.62				
	0.5	108.2	98.0	93.2	93.4	96.0	97.8	6.16				
	1.0	97.0	95.9	86.3	93.3	96.0	93.7	4.36				
	5.0	102.4	95.8	91.0	88.2	92.2	93.9	5.47				
Overall:							96.7	7.00	117.7	110.7	82.7	75.7
malathion	0.1	92.5	106.3	102.5	83.8	96.3	96.3	8.79				
	0.2	90.0	103.5	101.0	80.5	100.5	95.1	9.67				
	0.5	96.4	99.8	96.4	91.4	93.2	95.4	3.25				
	1.0	86.0	97.2	89.5	92.3	94.9	92.0	4.41				
	5.0	96.0	97.2	95.4	87.6	95.0	94.2	3.80				
Overall:							94.6	6.17	113.1	106.9	82.3	76.1
Chlorpyrifos	0.1	90.0	106.3	100.0	87.5	95.0	95.8	7.58				
	0.2	89.0	106.0	103.0	84.5	101.0	96.7	9.39				
	0.5	93.4	96.0	94.4	91.4	93.8	93.8	1.67				
	1.0	81.6	92.1	87.8	96.1	96.2	90.8	6.18				
	5.0	93.2	92.2	96.6	89.0	92.4	92.7	2.72				
Overall:							93.9	6.09	112.2	106.1	81.8	75.7
methidathion	0.1	102.5	113.8	100.0	93.8	102.5	102.5	7.23				
	0.2	104.0	116.0	98.0	91.5	109.0	103.7	9.50				
	0.5	95.0	93.4	94.8	89.4	92.6	93.0	2.26				
	1.0	89.2	103.0	91.3	98.4	98.5	96.1	5.69				
	5.0	93.4	102.0	96.6	89.8	95.2	95.4	4.48				
Overall:							98.1	7.18	119.7	112.5	83.8	76.6

Appendix II. Method Validation

Table 4. Method Validation Data (% recoveries) for Organophosphates in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
phosmet	0.1	91.3	90.0	98.8	108.8	90.0	95.8	8.13				
	0.2	107.5	98.0	91.5	106.5	112.5	103.2	8.36				
	0.5	97.0	93.2	98.0	102.8	95.0	97.2	3.64				
	1.0	86.1	109.0	96.2	101.0	108.0	100.1	9.40				
	5.0	104.0	99.8	97.0	93.2	93.0	97.4	4.65				
Overall:							98.7	7.10	120.0	112.9	84.5	77.4
Azinphos-methyl	0.1	95.0	93.8	98.8	95.0	97.5	96.0	2.05				
	0.2	101.5	104.0	104.5	91.5	112.5	102.8	7.55				
	0.5	100.4	103.8	92.8	98.8	95.2	98.2	4.32				
	1.0	107.0	115.0	101.0	116.0	110.0	109.8	6.14				
	5.0	95.8	101.6	94.2	99.6	100.6	98.4	3.20				
Overall:							101.0	6.81	121.5	114.7	87.4	80.6
Ethoprop	0.1	97.5	91.3	81.3	93.8	100.0	92.8	7.26				
	0.2	100.0	93.0	83.0	87.0	86.5	89.9	6.69				
	0.5	89.4	86.6	83.2	91.4	93.8	88.9	4.13				
	1.0	100.0	76.8	84.8	100.0	91.1	90.5	10.01				
	5.0	97.6	82.4	92.2	93.2	97.2	92.5	6.14				
Overall:							90.9	6.66	110.9	104.2	77.6	70.9
Phorate	0.1	92.5	86.3	82.5	102.5	86.3	90.0	7.86				
	0.2	92.0	84.0	82.5	81.5	78.0	83.6	5.19				
	0.5	78.8	82.2	78.6	86.4	87.4	82.7	4.12				
	1.0	93.8	71.0	87.6	89.8	91.4	86.7	9.07				
	5.0	92.6	76.6	70.6	83.6	91.2	82.9	9.41				
Overall:							85.2	7.37	107.3	99.9	70.4	63.1
Fonofos	0.1	93.8	86.3	82.5	107.5	85.0	91.0	10.13				
	0.2	97.0	93.0	86.0	88.0	83.0	89.4	5.59				
	0.5	81.8	84.0	80.8	89.2	90.2	85.2	4.28				
	1.0	95.9	70.1	89.8	90.5	87.4	86.7	9.81				
	5.0	95.0	79.6	90.4	86.2	97.4	89.7	7.11				
Overall:							88.4	7.38	110.6	103.2	73.6	66.3
E. Parathion	0.1	100.0	90.0	88.8	122.5	101.3	100.5	13.54				
	0.2	102.0	93.5	92.5	102.0	95.0	97.0	4.65				
	0.5	85.0	86.0	89.6	102.0	92.4	91.0	6.82				
	1.0	102.0	80.3	92.7	101.0	93.4	93.9	8.70				
	5.0	98.4	84.2	92.6	93.8	96.8	93.2	5.52				
Overall:							95.1	8.43	120.4	112.0	78.3	69.8
Phosalone	0.1	90.0	91.3	92.5	93.8	101.3	93.8	4.42				
	0.2	112.5	97.5	106.5	100.5	95.5	102.5	6.96				
	0.5	82.6	94.0	96.8	95.4	93.2	92.4	5.65				
	1.0	101.0	93.2	107.0	108.0	101.0	102.0	5.93				
	5.0	104.2	93.6	97.4	105.8	104.2	101.0	5.27				
Overall:							98.3	6.85	118.9	112.0	84.7	77.8

1. SD = standard deviation

Appendix II. Method Validation

Table 4. Method Validation Data (% recoveries) for Organophosphates in surface water										
Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]

2. UCL = upper control limit. LCL = lower control limit. Upper and lower control limits = mean ± 3SD
3. UWL = upper warning limit. LWL = lower warning limit. Upper and lower warning limits = mean ± 2SD

Appendix II. Method Validation

Table 5. Method Validation Data (% recoveries) for Carbamates in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
Aldicarb SO	0.1	63.8	66.0	72.6	72.4	57.1	66.4	6.48				
	0.2	63.0	65.0	66.0	67.5	64.0	65.1	1.75				
	0.5	68.2	72.6	72.6	61.0	67.2	68.3	4.78				
	1.0	62.6	67.0	64.2	68.3	60.1	64.4	3.31				
	4.0	68.5	68.3	62.0	69.0	68.8	67.3	2.99				
Overall:							66.3	4.09	78.6	74.5	58.1	54.0
Oxamyl	0.1	94.0	100.0	102.0	95.3	85.3	95.3	6.49				
	0.2	90.5	95.0	90.5	92.0	93.5	92.3	1.96				
	0.5	94.8	102.0	101.0	84.4	98.0	96.0	7.09				
	1.0	93.0	95.6	92.9	94.4	86.8	92.5	3.40				
	4.0	98.8	94.3	95.5	98.8	105.0	98.5	4.16				
Overall:							94.9	5.14	110.3	105.2	84.7	79.5
Mesurol SO	0.1	88.4	103.0	85.8	96.6	87.1	92.2	7.37				
	0.2	91.0	97.0	83.5	84.5	88.0	88.8	5.46				
	0.5	90.6	105.0	90.6	81.2	86.2	90.7	8.87				
	1.0	88.2	97.1	84.1	91.0	83.7	88.8	5.53				
	4.0	94.5	95.0	86.3	92.0	102.0	94.0	5.67				
Overall:							90.9	6.46	110.3	103.8	78.0	71.5
Aldicarb	0.1	91.9	92.8	77.0	76.4	73.4	82.3	9.28				
	0.2	77.5	72.0	65.0	73.5	78.5	73.3	5.37				
	0.5	84.8	88.0	75.2	79.0	70.0	79.4	7.23				
	1.0	76.6	84.2	74.5	68.1	61.8	73.0	8.52				
	4.0	93.5	86.5	86.0	84.5	101.0	90.3	6.92				
Overall:							79.7	9.52	108.2	98.7	60.6	51.1
Carbaryl	0.1	93.9	99.0	92.9	98.7	91.9	95.3	3.34				
	0.2	87.5	94.0	86.5	90.5	90.5	89.8	2.95				
	0.5	87.5	96.2	97.2	87.6	92.0	92.1	4.59				
	1.0	86.2	93.4	92.7	93.4	89.0	90.9	3.22				
	4.0	96.5	93.5	95.5	99.3	102.0	97.4	3.33				
Overall:							93.1	4.31	106.0	101.7	84.5	80.2
Aldicarb-SO2	0.1	96.2	79.3	85.0	96.4	92.4	89.9	7.49				
	0.2	79.0	91.5	99.5	95.2	92.5	91.5	7.66				
	0.5	91.8	96.0	87.2	94.8	84.0	90.8	5.08				
	1.0	94.7	98.4	95.2	105.0	92.0	97.1	4.99				
	4.0	89.3	94.3	93.0	97.3	99.0	94.6	3.79				
Overall:							92.8	6.12	111.1	105.0	80.5	74.4
Methomyl	0.1	96.3	69.2	72.8	98.6	92.9	86.0	13.86				
	0.2	77.0	88.5	90.5	96.0	86.5	87.7	6.95				
	0.5	83.2	91.6	90.2	86.2	81.2	86.5	4.44				
	1.0	92.3	84.3	92.2	91.4	76.1	87.3	7.08				
	4.0	89.5	91.0	93.8	98.0	98.5	94.2	4.04				
Overall:							88.3	7.98	112.3	104.3	72.3	64.4

Appendix II. Method Validation

Table 5. Method Validation Data (% recoveries) for Carbamates in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
3OH-Carbofuran	0.1	109.0	87.6	100.0	103.0	107.0	101.3	8.43				
	0.2	93.0	87.5	101.0	104.0	102.0	97.5	6.98				
	0.5	99.8	94.0	97.4	91.2	93.0	95.1	3.47				
	1.0	96.4	95.6	91.0	106.0	90.4	95.9	6.26				
	4.0	93.0	92.8	93.0	99.5	95.8	94.8	2.90				
Overall:							96.9	5.99	114.9	108.9	84.9	79.0
Mesurol-SO2	0.1	116.0	87.2	75.8	101.0	96.8	95.4	15.08				
	0.2	87.0	92.5	105.0	103.0	84.0	94.3	9.39				
	0.5	99.0	99.0	92.6	114.0	98.6	100.6	7.95				
	1.0	104.0	97.9	102.0	111.0	87.0	100.4	8.86				
	4.0	92.5	96.3	104.0	114.0	105.0	102.4	8.35				
Overall:							98.6	9.92	128.4	118.4	78.8	68.9
Carbofuran	0.1	96.0	72.4	68.9	93.0	93.3	84.7	12.96				
	0.2	80.5	91.5	93.0	99.0	89.0	90.6	6.74				
	0.5	87.0	87.6	84.0	84.2	109.0	90.4	10.54				
	1.0	99.3	88.0	91.2	97.1	80.4	91.2	7.54				
	4.0	92.5	92.5	94.5	98.5	98.3	95.3	2.98				
Overall:							90.4	8.76	116.7	108.0	72.9	64.1
Mesurol	0.1	112.0	84.0	80.3	96.0	97.3	93.9	12.52				
	0.2	82.5	92.5	100.0	97.5	89.0	92.3	6.95				
	0.5	95.8	94.4	79.0	93.8	87.0	90.0	7.03				
	1.0	98.8	96.0	84.0	100.0	86.6	93.1	7.31				
	4.0	91.3	92.3	93.5	103.0	99.0	95.8	5.00				
Overall:							93.0	7.70	116.1	108.4	77.6	69.9

1. SD = standard deviation
2. UCL = upper control limit. LCL = lower control limit. Upper and lower control limits = mean ± 3SD
3. UWL = upper warning limit. LWL = lower warning limit. Upper and lower warning limits = mean ± 2SD

Appendix II. Method Validation

Table 6. Method Validation Data (% recoveries) for Diazinon in surface water

Analyte	Spike Level ug/L	Recovery (% of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD[1]	UCL[2]	UWL[3]	LWL[3]	LCL[2]
Diazinon	0.08	90.0	100.0	97.5	101.3	88.8	95.5	5.77				
	0.2	82.0	99.0	93.5	77.0	90.5	88.4	8.86				
	0.5	91.8	97.4	89.4	89.4	85.4	90.7	4.40				
	1.0	83.0	93.7	82.4	84.7	85.9	85.9	4.55				
	5.0	93.8	93.6	88.2	83.6	89.0	89.6	4.24				
Overall:							90.0	6.22	108.7	102.5	77.6	71.4

1. SD = standard deviation
2. UCL = upper control limit. LCL = lower control limit. Upper and lower control limits = mean ± 3SD
3. UWL = upper warning limit. LWL = lower warning limit. Upper and lower warning limits = mean ± 2SD

APPENDIX III. ANALYTICAL METHODS

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Center for Analytical Chemistry
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Determination of Atrazine, Simazine, Diuron, Prometon, Bromacil, Prometryn, Hexazinone, Cyanazine, Metribuzin in River Water

Scope: This method is for the determination of atrazine, simazine, diuron, prometon, bromacil, prometryn, hexazinone, cyanazine, metribuzin in river water. The reporting limits for this method are: 0.05 ppb for atrazine, simazine, diuron, prometon, bromacil, prometryn, and 0.2 ppb for hexazinone, cyanazine, metribuzin.

Principal: Atrazine, simazine, diuron, prometon, bromacil, prometryn, hexazinone, cyanazine, metribuzin in river water are extracted with methylene chloride. The extract is evaporated to almost dryness, exchanged to methanol and passed through a conditioned Cl8 sep-pak for HPLC-UV and GC-NPD analyses.

Reagknts and Equipments:

Reagents:

1. Solvents: Acetonitrile, methanol, water (HPLC Grade)
   Methylene chloride (Pesticide quality or equivalent)
2. Sodium sulfate- (ACS) Granular, anhydrous
3. Individual stock standard solutions (1 mg/mL): Obtain standards from Standards Repository, California Department of Food and Agriculture, Center for Analytical Chemistry, 3292 Meadowview Rd. Sacramento, CA 95832

Equipments:

1. Rotary Evaporator
2. Nitrogen evaporator, Organomation Model # 112
3. Boiling flask - 500-mL, with standard taper to fit rotary evaporator
4. Separatory funnel - 1000-mL, with TFE stopcock
5. Graduated test tube - 15-mL
6. Syringe - 10-mL
7. Graduated cylinders - 1000-mL, 250-mL
8. Acrodisc®, 0.2 µm filter. Gelman Sciences
9. Balance - Analytical
10. Cl8 sep-pak

Analysis:

Sample Extraction:

1. Remove sample from the refrigerator and bring it to room temperature.
2. Mix the sample well, weigh 500.0 g of the sample and transfer into a 1000-mL separatory funnel.

Analysis:

Sample Extraction: (cont.)

3. Add 75 mL of methylene chloride to the separatory and gently shake for two minutes *with periodic venting to release excess pressure.* Allow the organic layer to separate from water layer. If the emulsion interface between layers occurs, the analyst must employ a mechanical technique such as stirring using a glass rod to complete the phase separation. Drain the bottom organic layer through a 75-cm funnel which contains glasswool and 40 g of sodium sulfate into a 500-mL boiling flask.
4. Repeat step # 3 two more times.
5. Evaporate the extract to just about dryness using a rotary evaporator set at 40 °C, and a vacuum of 20 inches Hg.
6. Transfer the residue from the flask into a 15-mL graduated test tube using 10 mL of methanol.
7. Condition a Cl 8 sep-pak with 5 mL of methanol, pass the 10 mL extract through the conditioned Cl8 sep-pak connected with a 0.2 um HPLC filter into a 15-mL graduated test tube.
8. Concentrate the extract from 10 mL to 1 mL using a Nitrogen evaporator set at 40 °C.
9. Mix well and transfer the extract into two microvials. One is for HPLC- *W* analysis and the other for GC-NPD analysis.

Instrument Condition:

HPLC-UV Parameter for atrazine, simazine, bromacil, diuron:

Instrument: HPLC HP-1050 with-a UV Variable Wavelength Detector.
Detector: *W* Variable Wavelength.
Wavelength: 280 nm.

Time table:	Wavelength
6.20 min.	**238** nm
13.80 min.	**280** nm

Column: Ultrasphere ODS 5 µm 4.6 mm x 25 cm.
Guard column: Ultrasphere ODS 5 µm 4.6 mm x 5 cm.
Mobile phase: Isocratic 40% ACN, 60% Water.
Flow rate: 1 mL per minute.
Injected volume: 20 µL.
Retention time:
Bromacil: 5.80 min.
Simazine: 6.60 min.
Atrazine: 10.30 min.
Diuron : 11.20 min.
Stop time: 20 min.

HPLC-UV Parameter for hexazinone, cyanazine; metribuzin:

Instrument: HPLC HP-1050.
Detector: *W* Variable Wavelength.
Wavelength: 238 nm.
Column: Ultrasphere ODS 5 µm 4.6 mm x 25 cm.
Guard column: Ultrasphere ODS 5 µm 4.6 mm x 5 *cm.*

Analysis:

Instrument Condition:

HPLC-UV Parameter for hexazinone, cyanazine, metribuzin:(cont.)

Mobile phase: Isocratic 30% ACN, 70% Water.

Flow rate: 1 mL per min.

Injected volume: 20 µL.

Retention time: Hexazinone: 8.68 min.
Cyanazine: 12.21 min.
Metribuzin: 13.54 min.

Stop time: 20 min.

GC-NPD parameter for atrazine, simazine, prometon, prometryn:

Instrument: GC HP- 6890.

Column: HP-35 35% Phenyl Methyl Siloxane 30 m x 0.53 mm x 1.0 um

Oven temperature: Initial temp: 70 °C
Initial time : 1.00 min
Ramps: 10 °C per min.
Final temp: 280 °C
Final time: 5 min.
Run time: 27 min.

Detector: NP Detector
Temperature: 300 °C
Hydrogen flow: 3.0 mL/min.
Air flow: 60.0 mL/min.
Mode: Constant column + make up (helium) = 30.0 mL/min.
Adjust offset: 50.00

Injector: Splitless
Temperature: 250 °C
Pressure: 4.1 psi
Injected volume: 3 µL.

Retention time: Prometon: 15.87 min.
Atrazine: 16.21 min.
Simazine: 16.3 1 min.
Prometryn: 17.76 min.

Calculations:

The results to be reported in part per billion (ppb) :

$$\text{ppb (ng/g)} = \frac{\text{ng/µL (from standard curve) x final volume (µL)}}{\text{Sample weight (g)}}$$

Method performance:

Quality Control:

1. Sample storage: All field samples shall be kept refrigerated at 4 °C until extracted.
2. Sample extraction: All extracts shall be kept frozen at -10 °C until analyzed.
3. Freezer, refrigerator and oven temperatures shall be monitored and recorded daily.

Method performance:

Quality Control: (cont.)

4. A 3-point or more calibration curve shall be obtained at the beginning and the end of each set of samples.
5. For each set of samples, one matrix blank, one distilled water blank, and one matrix spike shall be included, and each set of samples shall not contain more than twelve samples. Each sample shall be injected two times to determine reproducibility of the analysis.

Recovery data:

The analytical method was validated by preparing five sets of sample. Each set contained four different levels of spike, a distilled water blank, and a matrix blank. Each set was processed through the entire analytical method at a different time and the following results were tabulated:

For Atrazine:

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.100	0.099	99.0
0.100	0.098	98.0
0.100	0.103	103
0.100	0.096	96.0
0.100	0.096	96.0
0.500	0.400	80.0
0.500	0.458	91.6
0.500	0.472	94.4
0.500	0.504	101
0.500	0.476	95.2
2.000	2.168	108
2.000	1.860	93.0
2.000	2.133	107
2.000	1.890	94.5
2.000	1.975	98.8
6.000	6.340	106
6.000	6.420	107
6.000	6.440	107
6.000	6.400	107
6.000	6.474	108.

For Simazine:

0.100	0.108	108
0.100	0.098	98.0
0.100	0.099	99.0
0.100	0.099	99.0
0.100	0.125	125
0.500	0.447	89.4
0.500	0.468	93.6
0.500	0.503	101
0.500	0.529	106

Method performance:

Recovery data:

For Simazine:(cont.)

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.500	0.487	**97.4**
2.000	1.881	94.1
2.000	1.845	92.3
2.000	2.126	106
2.000	2.063	103
2.000	2.027	101
6.000	6.294	105
6.000	6.000	100
6.000	6.440	111
6.000	6.400	107
6.000	6.372	106
For Diuron:		
0.100	0.090	90.0
0.100	0.102	102
0.100	0.102	102
0.100	0.071	71.0
0.100	0.082	82.0
0.500	0.418	83.6
0.500	0.422	84.4
0.500	0.45 1	90.2
0.500	0.466	93.2
0.500	0.479	95.8
2.000	1.694	84.7
2.000	1.731	86.6
2.000	2.042	102
2.000	1.689	84.5
2.000	1.910	95.5
6.000	5.714	95.2
6.000	5.420	90.3
6.000	6.230	104
6.000	5.618	93.6
6.000	5.934	98.9
For Prometon:		
0.100	0.096	96.0
0.100	0.085	85.0
0.100	0.089	89.0
0.100	0.095	95.0
0.100	0.083	83.0
0.500	0.464	92.8
0.500	0.415	83.0
0.500	0.464	9i.8

Method performance:

Recovery data:

For Prometon:(cont.)

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.500	0.428	85.6
0.500	0.409	81.8
2.000	1.950	97.5
2.000	1.820	91.0
2.000	2.157	108
2.000	1.765	88.3
2.000	1.684	84.2
6.000	5.604	93.4
6.000	4.956	82.6
6.000'	5.894	98.2
6.000	5.110	85.2
6.000	4.958	82.6

For Prometryn:

0.100	0.104	104
0.100	0.091	91.0
0.100	0.099	99.0
0.100	0.086	86.0
0.100	0.086	86.0
0.500	0.492	98.4
0.500	0.441	88.2
0.500	0.511	102
0.500	0.436	87.2
0.500	0.433	86.6
2.000	1.992	99.6
2.000	1.921	96.1
2.000	2.119	106
2.000	1.807	90.4
2.000	1.665	83.3
6.000	6.000	100
6.000	5.336	88.9
6.000	6.190	103
6.000	5.350	89.2
6.000	5.228	87.1

For Bromacil:

0.100	0.099	**99.0**
0.100	0.098	**98.0**
0.100	0.087	87.0
0.100	0.094	94.0
0.100	0.089	89.0
0.500	0.458	91.6
0.500	0.475	95.0

Method performance:

Recovery data:

For Bromacil:(cont.)

Soiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.500	0.506	101
0.500	0.466	93.2
0.500	0.498	99.6
2.000	1.861	93.1
2.000	1.867	93.4
2.000	2.079	104
2.000	1.991	99.6
2.000	2.142	107
6.000	6.086	101
6.000	5.852	97.5
6 . 0 0 0	6.408	1 0 7
6.000	6.212	104
6.000	5.972	99.5

For Hexazinone:

0.300	0.298	99.3
0.300	0.299	99.7
0.300	0.298	99.3
0.300	0.307	102
0.300	0.365	122
0.500	0.428	85.6
0.500	0.453	90.6
0.500	0.524	105
0.500	0.444	88.8
0.500	0.534	107
2.000	1.927	96.4
2.000	1.951	97.6
2.000	2.009	101
2.000	2.066	103
2.000	2.100	105
6.000	5.984	99.7
6.000	5.530	92.2
6.000	5.980	99.7
6.000	5.900	98.3
6 . 0 0 0	6.244	104

For Cyanazine:

0.300	0.330	110
0.300	0.293	97.8
0.300	0.279	93.0
0.300	0.295	98.3
0.300	0.295	98.3
0.500	0.445	-89.0

Method performance:

Recovery data:

For Cyanazine:(cont.)

0.500	0.475	**95.0**
0.500	0.455	91.0
0.500	0.467	93.4
0.500	0.465	93.0
2.000	2.191	110
2.000	2.137	107
2.000	2.058	103
2.000	2.115	106
2.000	2.063	103
6.000	6.080	101
6.000	6.282	105
6.000	6.526	109
6.000	6.348	106
6.000	6.310	105

For Metribuzin:

0.300	**0.296**	**98.7**
0.300	**0.289**	**96.3**
0.300	0.287	**95.7**
0.300	0.259	86.3
0.300	0.271	90.3
0.500	0.434	86.8
0.500	0.458	91.6
0.500	0.462	92.4
0.500	0.438	87.6
0.500	0.452	90.4
2.000	1.863	93.2
2.000	1.859	93.0
2.000	1.827	91.4
2.000	1.937	96.9
2.000	1.777	88.9
6.000	5.400	90.0
6.000	5.862	97.7
6.000	5.836	97.3
6.000	5.358	89.3
6.000	5.984	99.7

Method detection limit:

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably. To determine the MDL, 7 replicated background samples were spiked at 0.050 μg (for atrazine, simazine, diuron, prometon, prometryn), and 0.200 μg (for hexazinone, cyanazine, metribuzin). The standard deviations derived from the spiked samples were used to calculate the MDL using the following equation:

Method performance:

Method detection limit: (cont.)

$$MDL = t S$$

where:

t is the Student t value for the 99% confidence level with n-l degrees of freedom (n-l, 1 - a = 0.99) which is 3.143, n represents the number of replicates which is 7.

S denotes the standard deviation obtained from replicate analyses.

The MDL and RL were tabulated as follow:

Chemical	Method detection limit (ppb)	*Reporting limit (ppb)
Atrazine	0.026	0.050
Simazine	0.014	0.050
Diuron	0.03 1	0.050
Prometon	0.026	0.050
Bromacil	0.025	0.050
Prometryn	0.023	0.050
Hexazinone	0.048	0.200
Cyanazine	0.040	0.200
Metribuzin	0.062	0.200

*Reporting limit (RL) refers to the level which quantitative results may be obtained usually 1-5 times the MDL

Dicussion:

Standards for quantitation of prometon, atrazine, simazine, and prometryn by GC/NPD must be made from the matrix blank extracts to compensate for the matrix enhanced response.

Confirmations:

All positve samples at reporting limits or above will be confirmed by APCI-LC/MS/MS.

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Appendix I: *Recovery data for determination of method detection limits*

	Spiked level (µg)	Results (µg)	Recovery (%)
For Atrazine:			
	0.050	0.048	96.0
	0.050	0.046	92.0
	0.050	0.047	94.0
	0.050	0.056	112
	0.050	0.046	92.0
	0.050	0.042	84.0
	0.050	0.048	96.0
For Simazine:			
	0.050	0.051	102
	0.050	0.053	106
	0.050	0.049	98.0
	0.050	0.056	112
	0.050	0.052	104
	0.050	0.05 1	102
	0.050	0.051	102
For Diuron:			
	0.050	0.045	90.0
	0.050	0.045	9 0 . 0
	0.050	0.046	92.0
	0.050	0.055	110
	0.050	0.053	106
	0.050	0.041	82.0
	0.050	0.047	94.0
For Bromacil:			
	0.050	0.040	80.0
	0.050	0.044	88.0
	0.050	0.040	80.0
	0.050	0.048	96.0
	0 . 0 5 0	0.042	84.0
	0.050	0.039	78.0
	0.050	0.049	98.0
For Prometon:			
	0.050	0.045	90.0
	0.050	0.050	100
	0.050	0.058	116
	0.050	0.048	96.0
	0.050	0.049	98.0
	0.050	0.053	106

Appendix I: *Recovery data for determination of method detection limits (cont.)*

For Prometryn:

Spiked level (µg)	Results (µg)	Recovery (%)
0.050	0.047	94.0
0.050	0.042	84.0
0.050	0.039	78.0
0.050	0.048	96.0
0.050	0.038	76.0
0.050	0.042	84.0
0.050	0.042	84.0

For Hexazinone:

0.200	0.187	93.5
0.200	0.196	98.0
0.200	0.191	95.5
0.200	0.180	90.0
0.200	0.184	92.0
0.200	0.184	92.0
0.200	0.201	101

For Cyanazine:

0.200	0.219	110
0.200	0.216	108
0.200	0.227	114
0.200	0.228	114
0.200	0.220	110
0.200	0.215	108
0.200	0.231	116

For Metribuzin:

0.200	0.204	102
0.200	0.195	90.0
0.200	0.196	98.0
0.200	0.205	103
0.200	0.216	108
0.200	0.185	92.5
0.200	0.197	98.5

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Original Date: March 1, 1992
Supersedes: none
Current Date: May 18, 1998
Method #:36.3

Dicamba, MCPA, 2,4-D, 2,4,5-T, Triclopyr and Bentazon in River Water by GC/MSD

Scope: This method is for the determination of Dicamba, MCPA 2,4-D, 2,4,5-T, Triclopyr and Bentazon in River water. The reporting limit of this method is 0.1 ppb for all compounds.

Principle: The water sample is acidified below **pH** 1. The protonated Dicamba, MCPA 2,4-D, **2,4,5-T,** Triclopyr and Bentazon are extracted with **1:1** petroleum ether : diethyl ether. The residues are derivatized with diazomethane, and analyzed by gas chromatography on **a** capillary column using a mass selective detector **(MSD).**

Reagents and Equipment:

Reagents:

1. Petroleum ether, grade suitable for pesticide residue analysis.
2. Diethyl ether, grade suitable for pesticide residue analysis.
3. Sulfuric acid, concentrated, A.C.S. reagent grade.
4. Hydrochloric acid, concentrated, A.C.S. reagent grade.
5. Ethanol, 95%.
6. Potassium hydroxide, **A.C.S** reagent grade.
7. N-methyl-**1-nitroso-p-toluenesulfonamide,** Aldrich 02,800-O
8. Sodium sulfate, anhydrous, suitable for pesticide residue analysis.
9. **Diazomethane** (see below)
10. Citral, 95% mixture of cis and trans.

Equipment:

1. Rotary evaporator **(Büchi/Brinkmann,** R110).
2. Nitrogen evaporator (Organomation Model # 12).
3. Distillation kit (Aldrich Z 10025-o)
4. **Hotplate** with magnetic stirrer, 10"x10"
5. Balance, Mettler PC 4400

PREPARATION OF DIAZOMETHANE:

Diazomethane is Explosive and Carcinogenic-use caution and protective measures (read MSDS)

Preparation of Diazomethane: continued

Diazomethane is prepared from N-methyl- 1-nitroso-p-toluenesul fonamide. Assemble a (cat #Z10,025-0) distillation apparatus according to the Aldrich Technical Information Bulletin number AL-I 3 1.

The reaction flask is placed in a 650C water bath on a hot plate with a magnetic stirring control. A 0.5-inch stirring bar is placed in the reaction flask and a l-inch stirring bar is placed in the water bath. Both magnetic bars should be stirring. Place a separatory funnel in the side arm of the Claisen adapter. Add 10 mL of 95% ethanol to a solution of 5 g KOH in 8 mL water in the reaction flask. Five grams of N-methyl- 1-nitroso-1-toluenesulfon amide crystals are carefully dissolved in. 100 mL ether and transferred into the separatory funnel. The crystals are moderately soluble in ether. Carefully open the stopcock of the funnel to allow the solution to drain into the reactiori flask at a slow rate of about 1 hour for the entire 100 mL solution. Add an additional 20 mL of ether to rinse the separatory funnel and drain it into the reaction flask. Diazomethane formed in the reaction is distilled, condensed and collected into'a 500 mL flask in an ice bath. After completing the distillation, transfer the diazomethane solution to a 4 ounce brown bottle with a Teflon-lined cap and store it in the freezer. This solution should be good for about a month in the freezer.

Analysis:

Sample Preparation:

1. Wash all glassware with IN HCl, rinse with deionized water and dry them in a 90°C oven.
2. Allow sample to equilibrate to ambient temperature. Measure 800 mL (or by weight) of the sample to be analyzed into a l-liter separatory funnel and record the volume or the weight to one decimal point.
3. Add 2.5 mL of the concentrated sulfuric acid to the water slowly and mix well.
4. Add 150 mL of 1 : I petroleum ether : diethyl ether (v/v). Shake it vigorously for 1.5 minutes. ***Vent frequently as pressure builds rapidly.***
5. Allow the phases to separate. Drain the aqueous layer into a l-liter beaker.
6. Pour the organic phase from the top of the separatory funnel into a 500-mL acid-washed beaker. Transfer the aqueous phase back to the separatory funnel.
7. Repeat steps 4 through 6 twice. Combine the extracts.
8 Add approximately 20 mL of anhydrous sodium sulfate to the solvent extracts and immediately stir with a Teflon rod to remove any water.
9. Pour the dried solvent to an acid-washed 500-mL boiling flask.
10. Rinse the beaker with 20 mL of the 1: 1 ether mix and combine in the flask.
11. Evaporate the solvent to about l-3 mL on a rotary evaporator at 35° C and 20 inches of vacuum.

Derivatization of the Residues;

1. Add 2 mL of the diazomethane solution to the residue in the flask.
2. Allow the reagent to contact the inside surface of the flask by swirling gently and let the reaction mixture sit in fume hood covered with aluminum foil for 20 minutes. (If the brownish-yellow color has disappeared within 20 minutes, add additional diazomethane and let the reaction mixture sit for another 20 minutes.

Derivatization of the Residues: continued

3. Evaporate the solvent and the excess reagent to just dryness at ambient temperature using a gentle stream of nitrogen.
4. Pipette 2 mL ethyl acetate into the flask and swirl. Make sure no significant solvent evaporation occurs before transferring the sample to an autosampler vial. Add 20 µL of 95 % Citral solution into the autosampler vial. The extract is ready for GC analysis.

Instrument Conditions:

Hewlett-Packard Model 6890 Gas Chromatograph equipped with a series 6890 Mass Selective Detector
Column: HP-5MS (5% Phenyl Methyl Siloxane), 30 m X 0.25 mm X 0.25 urn film.
Carrier: Helium, 8.8 psi
Column oven temperature:

Initial temperature:	700C hold for 1 .O minute
Program Rate	15°C/minute
Final	2500C hold for 4 minutes

Injector Temperature: 2500C
Transfer Line Temperature: 2800C
Ions Selected for SIM Acquisition:
Dicamba 188, 203, 234 start time: 6.0 min.
MCPA 141, 214, 216 start time: 9.1 min.
2,4-D 199, 234, 236 start time: 9.7 min.
Triclopyr 210, 212, 271 start time: 10.1 min.
2,4,5-T 209, 233, 268 start time: 10.6 min.
Bentazon 175, 2 12,254 start time: 11.4 min.

Retention time:

Dicamba	8.7 min.
MCPA	9.1 min.
2,4-D	9.7 min.
Triclopyr	10.2 min.
2,4,5-T	10.8 min.
Bentazon	11.6 min.

Volume Injected: 2 microliter

Calculation:

$$\text{Analyte (ppb)} = \frac{PA1}{PA2} \times \frac{FV}{W} \times SC \times 1000$$

Where:

PA1 = peak area of analyte from injected sample volume
PA2 = peak area of analyte standard
FV = final volume of sample extract (in mL)
W = sample weight (in grams)
SC = standard concentration (in ng/mL)

Method Performance:

Method Detection Limit(MDL)

Method Detection Limit refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. This was determined by fortifying seven aliquots of background water with 0.2 ppb of Dicamba, MCPA, 2,4--D, Triclopyr, 2,4,5-T and Bentazon then processing through the entire method along with a blank. The standard deviation derived from the 7 spiked samples was used to calculate the MDL using the following equation:

$$MDL = t\,S$$

where:

t is the Student **'t'** value for the 99% confidence level with n-l degrees of freedom (n-1, 1 - a = 0.99), which is 3.143. n represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses.

COMPOUND	S (standeviation, ppb)	MDL (ppb)
Dicamba	0.020	0.064
MCPA	0.014	0.045
2,4-D	0.013	0.041
Triclopyr	0.014	0.044
2,4,5-T	0.0196	0.062
Bentazon	0.01	0.031

Reporting Limit(RL)

It refers to the level above which quantitative results may be obtained. In this method the reporting Iimit is 0.1 ppb for all six compounds.

Recovery Data

The analytical method was validated by preparing 5 sets of spike samples. Each set contained four levels of spikes (0.2, OS, 2 and 10 ppb) and a matrix blank. the matrix was background water supplied by Dept. of Pesticide Regulation. All samples were processed through the entire analytical method. Recoveries of these compounds are summarized in the table below.

Method Validation Recovery Data:

Chemical Name	Spike Levels (ppb)	Recovery (%)	$\bar{x}$ (ppb)	Standard Deviation (ppb)	n
Dicamba	0.2	85.8	0172	0.022	5
	0.5	94	0.47	0.012	5
	2.0	106	2.11	0.130	5
	10.0	112	11.18	0.634	5

Recovery Data: continued

Chemical Name	Spike Levels (ppb)	Recovery. (%)	$\bar{x}$ (ppb)	Standard Deviation (ppb)	n
MCPA	0.2	104	0.207	0.014	5
	0.5	99.2	0.496	0.018	5
	2.0	105	2.106	0.187	5
	10.0	92.4	9.242	0.912	5
2,4-D	0.2	96.3	0.193	0.010	5
	0.5	90.6	0.453	0.035	5
	2.0	ioo	2.006	0.204	5
	10.0	82.3	8.234	0.932	5
Triclopyr	0.2	110	0.220	0.018	5
	0.5	111	0.554	0.033	5
	2.0	116	2.326	0.236	5
	10.0	95.6	9.560	0.911	5
2,4,5-T	0.2	99.2	0.198	0.004	5
	0.5	95.1	0.475	0.038	5
	2.0	103	2.05	0.099	5
	10.0	98.3	9.834	0.786	5
Bentazon	0.2	102	0.204	0.016	5
	0.5	94.0	0.470	0.055	5
	2.0	97	1.938	0.106	5
	10.0	95.1	9.512	0.972	5

Discussion:

Our experience indicated that with this method all glassware must be rinsed with acid to ensure **a** decent recovery.

The diethyl ether should be checked for any interfering peaks before using for extraction. If interfering peaks are present in the diethyl ether distillation is recommended.

Considerable peak sharpening was obtained by adding 20 µl of 95% Citral solution to -1 mL standard and sample extracts before analysis.

References:

Lee, Paul, *MCPA, DICAMBA and 2,4-D in River Water by GC/MSD,* 3-22-93, Environmental **Monitoring Method,** California Department of food and Agriculture.

UP DATED BY: Jean Hsu

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Original Date:01/10/97
Supersedes:none
Current Date:01/10/97
Method #:33.5

Determination of Glyphosate (N-phosphonomethyl glycine) in Runoff Water

Scope: This method is for the determination of glyphosate in runoff water by using HPLC with post-column derivatization and fluorescence detection. The detection limit and reporting limit for glyphosate using this procedure are 1.755 and 2.0 µg/L respectively.

Principles: A 500 mL sample of runoff water is acidified, and concentrated on a Chelex 100 (iron form) resin column. The residues, along with iron, are eluted with 6 N HCl. The $Fe(Cl)_4^-$, is removed from the residues by passage through an AG 1 x 8 resin column, an anion exchanger. The eluent is evaporated to dryness on a rotary evaporator. The glyphosate residue is redissolved in water and analyzed using HPLC with a post column derivatization system.

Reagents, Equipment and Instrument:

Reagents: All reagents must be suitable for pesticide residue analysis. Although some specific name brands are listed, equivalent supplies can be used:

1. Glyphosate, CAS # 1071-83-6, 1 .O mg/mL in water, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture).
2. Chelex® 100 resin, sodium form or iron form, 100-200 mesh, BioRad Laboratories, 2000 Alfred Nobel Dr., Hercules, Ca 94547. Contact the BioRad Laboratories for the sodium form to iron form conversion procedure.
3. Anion exchanger, AG® l-X&resin, Cl form, 200-400 mesh, BioRad Laboratories, 2000 Alfred Nobel Dr., Hercules, Ca 94547.
4. Deionized water, (DI water)
5. Hydrochloric acid.
6. Mobile phase: 0.005 M KH_2PO_4, pH 2.0, Pickering # K200.
7. Column Regenerant: Pickering RGO 19.
8. Hypochlorite diluent: pH 11.6, Pickering GA1 16, or dissolve 1.36 g KH_2PO_4, 11.6 g NaCl and 0.4 g NaOH in 500 mL DI water and dilute to 1000 mL with DI water.
9. Sodium hypochlorite: 5.25 % solution, Clorox™, or equivalent.
10. Hypochlorite solution: add 120 µL of 5.25% sodium hypochlerite to 1 L of hypochlorite diluent.
11. 0-phthalaldehyde diluent: Pickering GA104, pH 10.4, or dissolve 19.1 g of sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) in 1 .O L of DI water and adjust pH to 10.4 with

Sample Concentration with Chelex 100 Resin.

1. Mix sample well and then pour 500 mL into a beaker and record the weight.
2. Acidify the water sample with 6 N HCI to a pH of 2.0-2.3.
3. Add the acidified sample onto the column and elute at a rate of ~ 8 mL pei minute. (If column becomes plugged and will not drain the top surface of sediment can be stirred gently so as not to disturb the column.)
4. After the sample has eluted. rinse the column walls with 50 mL DI water. Next turn the stopcock wide open and rinse with 100 mL 0.1 N HCl.
5. Add 3 mL 6 N HCl carefully, so as not to disturb the column and elute at a rate of ~ 10 drops per minute. Discard the eluent. Add 4 more mL and discard.
6. Elute the glyphosate with 6 mL of 6 N HCl at a rate of ~ 10 drops per minute. Collect the eluent into a 150 mL beaker. Repeat the elution procedure two more times collecting all eluent.
7. Add an additional 5 mL 6 N HCl onto the column and collect the eluent into **the previously** collected fraction. Add 5 mL concentrated HCl to the eluent to ensure the eluted **iron complex is** in the negatively charged form.

Preparation of Anion exchange column:

1. Plug a column (1.1 cm ID x 30 cm) with glass wool and add ~ 5 mL of DI water.
2. Transfer 7 g of AG 1-X8 anion exchange resin into the column.
3. With the stopcock wide open rinse the column with about 20-50 mL DI water.
4. Rinse the column twice with ~ 30 mL of 6 N HCl.
5. With the stopcock wide open. rinse the column with ~ 10 mL of 6 N HCl shortly before applying the sample.

Sample clean-up with an anion exchange column: AC 1x8 Resin

1. Transfer the sample onto the anion exchange column and elute with stopcock wide open. Collect the efuent into a 250 mL flat bottom flask.
2. Rinse the sample container with ~ 6 mL 6 N HCl and apply to the column.
3. Rinse the sample container with an additional 6 mL 6 N HCl and apply to the column.
4. Collect the rinse eluents into the corresponding 250 mL flask.

Concentration of the sample:

1. Evaporate the sample just to dryness on a rotary vacuum evaporator in a 65 °C water bath with 28-29 inches of vacuum. **To avoid sudden bumping, immerse the flask approximately 2-3 cm into the water for the first 3-5 minutes of evaporation.**
2. Place the flask on a 90 °C steam bath under a gentle stream of N_2 for 2-3 minutes to dry completely, then remove from the steam bath.
3. After the flask has cooled to room temperature, rinse down the sides of the flask with 2-mL DI water. Filter extract through a 0.2 µm filter into a 2-mL auto sampler vial for analysis.

Instrument Conditions:

Instrument: Perkin Elmer Series 4 HPLC with column oven and a Pickering post column system
Detector: Fluorescence: Excition, 340 nm & Emission, 465 nm
Column: Pickering Potassium Cation Exchange 4 mm x 150 mm x 8 µm

Instrument Conditions:continued

Guard Column: Glyphosate guard column k^+ form 3 x 20 mm
Column Temperature: 55 °C
Mobile Phase:
Eluent A: 0.005 M KH_2PO_4, pH 2.0
Eluent B: Column regenerent, or RG019

Time (min.)	Eluent A %	Eluent B %
1.0	100	0.0
15	100	0.0
2	0.0	100
6	100	0.0

Flow Rate: 0.4 mL/min.
Injection volume: 10 µL

Post Column System: Pickering
Derivatization Reagents: Hypochlorite solution & OPA solution
Flow Rate: 0.3 mL/min
Reaction Temperature: 3 1 °C
Retention time: Glyphosate, 8.6 ± 0.2 minutes

Calculation:

$$\mu g/L \text{ glyphosate} = \frac{\text{peak area of sample x final volume (mL) x 1000 (g/L)}}{\text{response factor x sample weight(g)}}$$

$$\text{Where: response factor} = \frac{\sum(\text{peak area}_n / \text{std concentration}_{n\ ug/mL})}{n}$$

n = number of standards

Method Performance:

Quality Control:

1. A 4'point calibration curve of 0.5, 1 .O, 2.0, and 4.0 ng/µL glyphosate was obtained at the beginning and the end of each set of samples.
2. Each sample shall be injected two times to insure reliability of the analysis. If the signal of a sample is greater than that of the highest standard in the calibration curve, dilute the sample. Reinject the diluted sample together with standards twice more. A sample set is usually comprised of 8 samples, a blank and a spike.

Recovery Data:

The analytical method was validated using 4 sets of spike samples. Each set contained 3 levels of spikes and a matrix blank. The matrix background water was supplied by Dept. of Pesticide Regulation. All samples were processed through the entire analytical method.

Analyte	Spike Level (µg/L)	Results (µg/L)	Recovery (%)
Glyphosate	4.0	2.35	58.8
		2.96	74.0
		2.37	59.3
		2.72	68.0
	20	14.9	74.9
		14.4	72.0
		14.8	74.0
		16.2	81.0
	100	81.7	81.7
		70.1	70.1
		78.4	78.4
		74.1	74.1

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. To determine the MDL, 7 samples each containing 500 mL of background surface water were spiked with 4 ug glyphosate. The standand deviation derived from the 7 spikes was used to calculate the MDL using the following equation:

$$MDL = S\,t$$

where:

t is the student's "t" value for the 99% confidence level with n-l degrees of freedom (n-l ,1-α = 0.99). n represents the number of replicates
S denotes the standard deviation obtained from replicate analyses.

Method Detection Limit (MDL): continued

Spike Recoveries for MDL Determination

Spike	Recovery µg/L
1	5.29
2	4.97
3	5.86
4	5.37
5	4.59
6	5.83
7	6.20

The standard deviation ascertained for glyphosate is 0.558 µg/L
The MDL is 1.755 µg/L for glyphosate.

Reporting Limit (RL):

RL refers to the level above which quantitative results may be obtained. The MDL was used as a guide for determining the RL. The reporting limit for this method is 2.0 µg/L which is the value obtained for the MDL rounded to the nearest whole number.

Discussion:

AG 1-X8 resin was successfully regenerated in our study. This was acomplished by adding approximately 30 mL of DI water to the column to wash off the iron. If the column starts to change back to its orginial color regeneration is possible. Let the water drain ~ half way down and then add ~ 10 mL of 6 N HCI. The column should turn a light yellow color. Let this solution drain completely and then wash the column with ~ 30 mL of DI water. The column should be back to the orginal color. Continue with step *4* in *Preparation of Anion Exchange Column* and the column is ready to reuse. The chemist must be alert to any adverse effects after several times of reuse.

The HPLC column should be stored in regenerant solution when not in use to prolong the life of the column. The column may need to be treated with Restore occassionaly when peak shape starts to broaden. Treat the column with Restore for 60 minutes, then rinse with the mobile phase for 30 minutes and try the column again. If this does not work it may be necessary to replace the column.

Irreversible damage to the column may be caused by solvent passing through the analytical column or running the column at high flow rates.

References:

1. Lee, Paul, *Determination of Glyphosate (N-phosphonomethyl glycine) and AMPA (Aminomethyl phosphonic acid) in Well Water by HPLC, with Post-column Derivatization and Fluorescence Detection*, 1 o-30-95, Enviromental Monitoring Methods, California Department of Food and Agriculture.

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3. Jerry R. Steinmetz *"Analytical Methodfor Glyphosate and AMPA in Raw Agricultural Commodities, and Their Processed Fractions, Document #Res-008-90"*, Environmental Science Department, Monsanto Company, 700 Chesterfield Parkway North, St. Louis, Missouri 63 198. Fax Number: (3 14) 537-6134.

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Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography

Scope: This method is for the determination of organophdsphate pesticides in surface water. The reporting limit (RL) of the method for diazinon and chlorpyrifos is 0.04 µg/L. Dichlorvos (DDVP), dimethoate, methyl parathion, malathion, ethyl parathion, methidation, phosmet, phosalone, azinphos-methyl, thimet, ethoprop and fonofos have a RL of 0.05 µg/L.

Principle: The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed using a gas chromatograph equipped with a flame photometric detector (FPD).

Reagents, Equipment and Instruments:

Reagents:

1. Methylene Chloride (pesticide residue grade)
2. Acetone (pesticide residue grade)
3. Sodium sulfate, anhydrous
4. Organophosphate pesticide stock standard solutions (1mg/mL): Obtain standards from Center for Analytical Chemistry, CDFA

Equipment:

1. Rotary evaporator (Büchi/Brinkmann)
2. Nitrogen evaporator (Organomation Model # 112)
3. Vortex-vibrating mixer
4. Conical test tube with glass stopper, 15 mL, graduated
5. Separatory funnel, 2 L
6. Boiling flask, 500 mL
7. Whatman filter paper #4, 15 cm
8. Funnel, long stem, 60 mm
9. Disposable Pasteur pipettes, 5.75 inches
10. Balance (Mettler PC 4400)

Instrument:

Hewlett Packard 5890 Series II GC with FPD and a HP-l, methyl silicone gum megabore column(10 m x 0.53 mm x 2.65 µm).

Analysis:

Sample Extraction:

1. Remove water samples from refrigerator and allow them to come to room temperature.
2. Record weight of water by weighing sample bottle before and after water has been transferred into a separatory fimnel.
3. Extract sample by shaking with 100 mL of methylene chloride for 2 minutes. ***Vent frequently to relieve pressure.***
4. After the phases have separated, drain the lower methylene chloride layer through 20 g of anhydrous sodium sulfate, into a boiling flask.
5. Repeat steps 3 & 4 two more times using 80 mL of methyiene chloride each time.
6. After draining the final extraction, rinse the sodium sulfate with 25 mL of methylene chloride.
7. Evaporate the sample extract to just dryness on a rotary evaporator using a 35 °C water bath and approximately 20 inches Hg vacuum.
8. Add 5 mL of acetone and swirl to dissolve the residue in the flask. Transfer the extract to a calibrated 15-mL graduated test tube.
9. Rinse flask 2 more times, each time with 2 mL of acetone and transfer each rinse to the same t&t tube.
10. Under a gentle stream of nitrogen with no heat applied, evaporate the extract to a volume slightly less than 1 mL. Then, bring to a final volume of 1 .0 mL with acetone.
11. Submit extract for GC analysis.

Instrument Conditions

Primary Analysis:

Instrument: Hewlett Packard 5890 Series II GC with FPD
Column: HP-l, methyl silicone gum, 10 m x 0.53 mm x 2.65 µm
Carrier gas: helium, column flow rate 20 mL/min.
Injector temperature: 220 °C
Detector temperature: 250 °C
Injection volume: 3 µL
Column oven temperature:

Initial temperature:	150 °C held for 1 minute
Ramp rate 1:	10 °C/min.
Final temperature:	200 °C held for 2 minutes
Ramp rate 2:	20 °C/min.
Final temperature:	250 °C held for 5 minutes

Confirmation Analysis:

Instrument: Hewlett Packard 5890 Series II GC with FPD
Column: HP-17, 50% phenyl methyl silicone gum, 10 m x 0.53 mm x 2.0µm
Injector temperature: 220 °C
Detector temperature: 250 °C
Injection volume: 3 µL
Column oven temperature:
Same as primary analysis conditions.

Analysis: continued

Retention times:

Chemicals	HP-1	HP-17
DDVP	0.68	1.10
Dimethoate	3.25	6.22
Diazinon	4.10	5.36
Methyl Parathion	4.75	7.50
Malathion	5.51	8.21
Chlorpyrifos	5.75	7.93
Methidathion	6.67	10.36
Phosmet	10.16	13.71
Azinphos-Methyl	10.72	15.14
Ethoprop	2.67	3.96
Thimet	3.16	4.56
Fonofos	3.89	5.62
Ethyl parathion	5.70	8.38
Phosalone	10.81	13.49

Calculations:

$$\mu g/L = \frac{\text{(peak ht of sample) (std. conc.) (std. vol. injected) (final vol. sample, mL) (1000 } \mu L/mL)}{\text{(peak ht. std) (sample vol. injected) (sample wt., g)}}$$

Method Performance:

Quality Control:

A three point calibration curve (0.04 ng/μL, 0.08 ng/μL and 0.2 ng/μL) was obtained at the beginning and the end of each set of samples. Each samples shall be injected two times to insure reliability of the analysis. If a sample signal is greater than the highest standard, dilute the sample. Reinject the diluted sample and standards twice more.

Recovery Data:

Method validation was made by spiking 1000 g of American River water with five different levels of spikes (0.08, 0.2, 0.5, 1.0, and 5.0 μg/L) and a blank for five different days (see appendix I). Recoveries of the analytes are summarized below:

Recovery of Organophosphate Pesticides in Surface Water

Organophosphate Pesticides	Spike level (μg/L)	# Spikes (n)	Mean Recovery (%)	Deviation (Based on % Recovery)
DDVP	0.08	5	90.5	6.94
	0.2	5	90.3	6.19
	0.5	5	85.0	10.4
	1.0	5	82.9	3.83
	5.0	5	87.6	8.64

Method Performance: continued

Organophosphate Pesticides	Spike level (µg/L)	Spike (n)	Mean Recovery (%)	Standard Deviation (Based on % Recovery)
Dimethoate	0.08	5	102	3.14
	0.2.	5	98.0	9.15
	0.5	5	103	5.11
	1.0	5	96.9	9 . 0 3
	5.0	5	96.2	5.58
Diazinon	0.08	5	**95.5**	5.77'
	0.2	5	88.4	8.86
	0.5	5	90.7	4.40
	1.0	5	85.9	4.55
	5.0	5	89.6	4.24
Methyl Par&on	0.08	5	**97.8**	**9.50**
	0.2	5	101	8.62
	0.5	5	97.8	6.16
	1.0	5	93.7	4.36
	5.0	5	94.0	5.44
Malathion	0.08	5	**96.3**	**8.79**
	0.2	5	95.1	**9.67**
	0.5	5	95.4	3.25
	1.0	5	92.0	4.41
	5.0	5	94.3	3.83
Ethyl parathion	0.08	5	101	13.5
	0.2	5	97.0	4.65
	0.5	5	91.0	6.82
	1.0	5	93.7	8.55
	5.0	5	93.2	5.52
Chlorpyrifos	0.08	5	**95.8**	7.58
	0.2	5	**96.7**	9.39
	0.5	5	**93.8**	1.67
	1.0	5	**90.8**	6.18
	5.0	5	**92.6**	2.71
Methidathion	0.08	5	102	7.23
	0.2	5	104	9.50
	0.5	5	93.0	2.26
	1.0	5	96.1	5.66
	5.0	5	95.4	4.49.

Method Performance: continued

Organophosphate Pesticides	Spike level (µg/L)	Spike (n)	Mean Recovery (%)	Standard Deviation (Based on % Recovery)
Phosmet	0.08	5	95.8	8.13
	0.2	5	103	8.36
	0.5	5	97.2	3.64
	1.0	5	99.9	9.30
	5.0	5	97.3	4.66
Azinphos-Methyl	0.08	5	96.0	2.05
	0.2	5	103	7.55
	0.5	5	98.2	4.32
	1.0	5	110	6.03
	5.0	5	98.4	3.20
Phosalone	0.08	5	98.3	4.42’
	0.2	5	103	6.96
	0.5	5	92.4	5.65
	1.0	5	102	5.89
	5.0	5	101	5.30
Thimet	0.08	5	90.0	7.86
	0.2	5	83.6	5.19
	0.5	5	82.7	4.12
	1.0	5	86.7	9.07
	5.0	5	82.9	9.45
Ethoprop	0.08	5	92.8	7.26
	0.2	5	89.9	6.69
	0.5	5	88.9	4.13
	1.0	5	90.6	10.1
	5.0	5	92.5	6.15
Fonofos	0.08	5	91.0	10.1
	0.2	5	89.4	5.59
	0.5	5	85.2	4.28
	1.0	5	86.7	9.81
	5.0	5	89.7	7.09

Method Performance: continued

Method Detection Limit:

Data used to calculated the method detection limit (MDL) is in appendix II. The MDL is as follows:

Compound	STDEV (µg/L)	MDL (µg/L)
DDVP	0.003	0.009
Ethoprop	0.005	0.016
Dimethoate	0.003	0.009
Thimet	0.005	0.016
Fonofos	0.004	0.013
Diazinon	0.003	0.009
M. Parathion	0.003	0,009
Malathion	0.004	0.013
E. Parathion	0.003	0.009
Chlorpyrifos	0.004	0.013
Methidathion	0.008	0.025
Phosmet	0.004	0.013
Azinphos methyl	0.008	0.025
Phosalone	0.004	0,013

These are the minimum concentrations of the above compounds that can be reported with 99% confidence. The method detection limit (MDL) was computed based on the following procedure:
a) Prepared 7 replicates of the analytes at 0.05 µg/L using American River water.
b) Compute the MDL as follows:

$$MDL = t \times S$$

where;
t is the Student 't' value for the 99% confidence level with n-l degrees of freedom (n-1, $1 - \alpha = 0.99$). n represents the number of replicates.
S denotes the standard deviation obtained from replicate analyses.

Reporting Limit

The reporting limits (RL) for diazinon and chlorpyrifos are 0.04 µg/L. For the remaining compounds, the RL is 0.05 µg/L. The MDL is used as a guide to determine the RL for this method. The RL is 1 - 5 times the MDL.

Discussion:

Methidathion, phosmet, azinphos methyl and phosalone compounds were enhanced by the matrix used in the validation. To eliminate the matrix problem, spike samples at level of 0.08, 0.2 and 0.5 ppb were calculated using standards prepared in blank matrix extract. The 0.08 and 0.2 µg/mL standards were prepared by pipetting 1 mL of background matrix into different test tubes and evaporating them to dryness in a nitrogen evaporator at 40 °C. Then, 1 ml of the working

Discussion: continued

standard was pipetted into the test tube separately and mixed well. These standards were used to calculate the 0.08 and 0.2 µg/L spikes. The 0.5 µg/mL standard was prepared by pipetting 0.2 mL of background matrix extract into a test tube and evaporating it to dryness in a nitrogen evaporator at 40 °C. Then, 1 mL of 0.5 µg/mL working standard was pipetted into the test tube and mixed well. This standard was used to calculate the 0.5 µg/L spikes. The 1 .O and 5.0 µg/L spikes were calculated using standards without addition of background matrix extract.

Several peaks were noted in the chromatograms of the blank and samples that had the same retention times as those of phosmet, phosalone and azinphos-methyl. These' interferences may have been caused by impurities in the sodium sulfate used. The interfering peaks disappeared after the sodium sulfate used in extraction had been washed with methylene chloride. To avoid these interferences, it is recommended that the sodium sulfate should be washed with methylene chloride prior to use.

Reference:

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2. ***Method 8141, Organophosphorus Pesticides, Capillary Column.*** EPA Test Methods for Evaluating Solid Waste. Revised Methods, 1987.

3. ***EPA Method 507, Pesticides, Capillary Column.*** EPA Test Method for Drinking water and raw source water, 1987.

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Day 1 - OP's Melthod Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.064	0.164	0.437	0.817	4.57
Cygon	ND	0.085	0.201	0.527	0.918	4.88
Diazinon	ND	0.072	0.164	0.459	0.830	4.69
M. Parathion	ND	0.085	0.209	0.541	0.970	5.12
Malathion	ND	0.074	0.180	0.482	0.860	4.80
Dursban	ND	0.072	0.178	0.467	0.816	4.66
Supracide	ND	0.082	0.208	0.475	0.892	4.67
Imidan	ND	0.073	0.215	0.485	0.861	5.20
Guthion	ND	0.076	0.203	0.502	1.07	4.79
Ethoprop	ND	0.078	0.200	0.447	1.00	4.88
Timet	ND	0.074	0.184	0.394	0.938	4.63
Fonofos	ND	0.075	0.194	0.409	0.959	4.75
E! Parathion	ND	0.080	0.204	0.425	1.02	4.92
Zolone	ND	0.072	0.225	0.413	1.01	5.21
Day 2 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.079	0.198	0.500	0.879	5.01
Cygon	ND	0.080	0.169	0.544	1.09	5.22
Diazinon	ND	0.080	0.198	0.487	0.937	4.68
M. Parathion	ND	0.084	0.211	0.490	0.959	4.79
Malathion	ND	0.085	0.207	0.499	0.972	4.86
Dursban	ND	0.085	0.212	0.480	0.921	4.61
Supracide	ND	0.091	0.232	0.467	1.03	5.10
Imidan	ND	0.072	0.196	0.466	1.09	4.99
Guthion	ND	0.075	0.208	0.519	1.15	5.08
Ethoprop	ND	0.073	0.186	0.433	0.768	4.12
Timet	ND	0.069	0.168	0.411	0.710	3.83
Fonofos	ND	0.069	0.186	0.420	0.701	3.98
E. Parathion	ND	0.072	0.187	0.430	0.803	4.21
Zolone	ND	0.073	0.195	0.470	0.932	4.68

Dav 3 - **OP's Method Validation**						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.075	0.177	0.422	0.783	4.07
Cygon	ND	0.080	0.205	0.477	0.851	4.64
Diazinon	ND	0.078	0.187	0.447	0.824	4.41
M. Parathion	ND	0.079	0.203	0.466	0.863	4.55
Malathion	ND	0.082	0.202	0.482	0.895	4.77
Dursban	ND	0.080	0.206	0.472	0.878	4.83
Supracide	ND	0.080	0.196	0.474	0.913	4.83
Imidan	ND	0.079	0.183	0.490	0.962	4.85
Guthion	ND	0.079	0.209	0.464	1.01	4.71
Ethoprop	ND	0.065	0.166	0.416	0.848	4.61
Timet	ND	0.066	0.165	0.393	0.876	3.53
Fonofos	ND	0.066	0.172	0.404	0.898	4.52
E. Parathion	ND	0.071	0.185	0.448	0.927	4.63
Zolone	ND	0.074	0.213	0.484	1.07	4.87
Day 4 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.073	0.179	0.409	0.811	3.91
Cygon	ND	0.079	0.188	0.517	1.02	4.49
Diazinon	ND	0.081	0.154	0.447	0.847	4.18
M. Parathion	ND	0.066	0.171	0.467	0.933	4.41
Malathion	ND	0.067	0.161	0.457	0.923	4.38
Dursban	ND	0.070	0.169	0.457	0.961	4.45
Supracide	ND	0.075	0.183	0.447	0.984	4.49
Imidan	ND	0.087	0.213	0.514	1.01	4.66
Guthion	ND	0.076	0.183	0.494	1.16	4.98
Ethoprop	ND	0.075	0.174	0.457	1.00	4.66
Timet	ND	0.082	0.163	0.432	0.898	4.18
Fonofos	ND	0.086	0.176	0.446	0.905	4.31
E. Parathion	ND	0.098	0.204	0.510	1.01	4.69
Zolone	ND	0.075	0.201	0.477	1.08	5.29

Day 5 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.071	0.185	0.356	0.857	4.34
Cygon	ND	0.083	0.217	0.501	0.974	4.83
Diazinon	ND	0.071	0.181	0.427	0.859	4.45
M. Parathion	ND	0.077	0.212	0.480	0.960	4.61
Malathion	ND	0.077	0.201	0.466	0.949	4.75
Dursban	ND	0.076	0.202	0.469	0.962	4.62
Supracide	ND	0.082	0.218	0.463	0.985	4.76
Imidan	ND	0.072	0.775	0.475	1.08	4.65
Guthion	ND	0.078	0.225	0.476	1.10	5.03
Ethoprop	ND	0.080	0.173	0.469	0.911	4.86
Timet	ND	0.069	0.156	0.437	0.914	4.56
Fonofos	ND	0.068	0.166	0.451	0.874	4.87
E. Parathion	ND	0.081	0.190	0.462	0.934	4.84
Zolone	ND	0.081	0.191	0.466	1.01	5.21

Apendix II

MDL - OP's Method											
	Results in ppb										
Analyte	Blank	Spk 1	Spk 2	Spk 3	Spk 4	Spk 5	Spk 6	Spk 7	STDEV	MDL (ug/L)	RL (ug/L)
DDVP	0.000	0.040	0.035	0.046	0.040	0.040	0.042	0.039	0.003	0.009	0.05
ETHOPROP	0.000	0.043	0.049	0.036	0.043	0.051	0.043	0.047	0.005	0.016	0.05
CYGON	0.000	0.053	0.050	0.052	0.047	0.046	0.050	0.047	0.003	0.009	0.05
TIMET	0.000	0.038	0.050	0.038	0.044	0.049	0.041	0.047	0.005	0.016	0.05
FONOFOS	0.000	0.040	0.044	0.036	0.043	0.049	0.044	0.046	0.004	0.013	0.05
DIAZINON	0.000	0.052	0.044	0.050	0.045	0.043	0.047	0.045	0.003	0.009	0.04
M. PARATHION	0.000	0.053	0.048	0.046	0.046	0.045	0.050	0.044	0.003	0.009	0.05
MALATION	0.000	0.054	0.048	0.051	0.044	0.043	0.049	0.044	0.004	0.013	0.05
E. PARATHION	0.000	0.046	0.052	0.045	0.047	0.052	0.048	0.049	0.003	0.009	0.05
DURSBAN	0.000	0.052	0.046	0.051	0.043	0.042	0.050	0.043	0.004	0.013	0.04
SUPRACIDE	0.000	0.069	0.052	0.055	0.049	0.046	0.052	0.045	0.008	0.025	0.05
IMIDAN	0.000	0.079	0.073	0.080	0.073	0.068	0.071	0.071	0.004	0.013	0.05
GUTHION	0.000	0.071	0.061	0.078	0.061	0.058	0.057	0.056	0.008	0.025	0.05
ZOLONE	0.000	0.044	0.052	0.052	0.050	0.056	0.055	0.056	0.004	0.013	0.05

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Method #: 11.3
Original Date: March 10,1998
Revised Date: Nov 5, 1998

HPLC Determination of Carbamates in Surface Water

Scope: This method is for the determination of Aldicarb Sulfoxide, Oxamyl, Mesurol Sulfoxide, Aldicarb, Carbaryl, Aldicarb Sulfone, Methomyl, 3-Hydroxycarborfuran, Mesurol Sulfone, Carbofuran and Mesurol in surface water. The reporting limit of this method is 0.05 ppb.

Principle: Pesticides in water are extracted with methylene chloride. After evaporating the methylene chloride, the extracted residues are redissolved in methanol and separated by HPLC. The analyte is derivatized with OPA in a post column reaction and detected with a fluorescence detector.

Reagents, Equipment and Instrument:

Reagents.

1. Carbamate Standards, 1 .O mg/mL in methanol, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture)
2. Methylene chloride, pesticide residue grade
3. Methanol, pesticide residue grade
4. Water, HPLC grade
5. Acetonitrile, HPLC grade
6. Hydrolysis Reagent C47™, Pickering Laboratories, part# CB 130
7. 0-Phthalaldehyde, Pickering Laboratories, part' 0 120
8. Thiofluor™, N,N-Dimethyl-2-mercaptoethylamine-Hydrochloride, Pickering Laboratories, part# 3700-2000
9. 2-Mercapto-ethanol, Pickering Laboratories, part# 3700-l 300
10. O-Phthalaldehyde diluent, pH 9.1, Pickering Laboratories, part# CB9 10
11. OPA Reagent: Dissolve 100 mg of 0-Phthalaldehyde in 10 mL methanol. Add this mixture to 950 mL 0-Phthalaldehyde diluent and mix well. Pour the solution into the reagent reservoir and add 2 g of Thiofluor or 1 mL of 2-Mercapto-ethanol directly into it.
12. Sodium sulfate, anhydrous, granular, ACS 1 O-60 mesh

Equipment:

1. Separatory funnels, 250 mL
2. Boiling flasks, flat-bottomed, 24/40 joints, 500 mL
3. Rotary evaporator, Büchi-Brinkmann, Model R 110
4. Centrifuge tubes, round bottom
5. Nitrogen evaporator, Organomation, Model 12

Equipment: continued

6. Vortex mixer, Thermolyne, Model 37600
7. Acrodisc®, Gelman, 25 mm x 0.2 pm, disposable filter

Instrument:

1. HPLC: Hewlett-Packard 1090 Liquid Chromatograph with the ChemStation
2. Post column system: Pickering Laboratories PCX5 100 Post-Column Derivatization
3. Fluorescence Detector: Hewlett-Packard 1046-A Programmable Fluorescence Detector
4. Analytical column: Pickering Laboratories "Carbamates Analysis" C 18, 4.6 mm x 25 cm x 5 µm

Analysis:

Sample Extraction:

1. Remove samples from refrigerated storage and allow them to come to room temperature (± 5 °C).
2. Shake each sample and weigh out 100 grams by difference. Place this aliquot into a separatory funnel.
3. Extract samples by adding 100 mL of methylene chloride and shaking vigorously for one minute. **Vent frequently to relieve pressure.**
4. After phase separation, drain the methylene chloride into a 500 mL boiling flask.
5. Repeat steps 3 and 4 two more times with 100 mL of methylene chloride each.
6. Concentrate the extract to 2 ~ 3 mL on a rotary evaporator using 30 ~ 35 °C water bath and a vacuum of 15 inches Hg.
7. Add ~ 1 gram anhydrous sodium sulfate to remove any water droplets.
8. Filter the extract through a .2 pm Acrodisc® unit and collect the filtrate in a round bottom centrifuge tube.
9. Rinse the flask two times with 2 mL of methylene chloride each. Filter through the same Acrodisc® and collect the rinse in the same centrifuge tube.
10. Place extract in a nitrogen evaporator with water bath set at 35 °C and evaporate just to ~ 200 µL under a gentle stream of nitrogen.
11. Add 600 µL of methanol and mix contents by vortexing for about 15 seconds.
12. Place extract in a nitrogen evaporator with water bath set at 35 °C and evaporate to ~ 100 µL
13. Transfer the contents into an autosampler vial insert precalibrated to 200 µL . Wash the tube with ~ 60 µL methanol and transfer to the same insert. Add methanol to the insert until the volume reaches 200 µL. Use a pasteur pipet to mix contents of the insert gently by sucking in and out.
14. Analyse the extract by HPLC.

Instrument Conditions:

Mobile phase:

Time (min.)	Water %	Acetonitrile %
0	100	0
1	100	0
16	30	70

Instrument Conditions:continued

18	*30*	70
21	100	0
23	100	0

Flow: 1 .OmL/min.
Injection volume: 25 µL
Post column system: Pickering Laboratories PCX5 100 Post-Column Derivatization
Column Temperature = 42 °C
Rcagcnt 1 = Hydrolysis Reagent C47™, Reactor Temperature = 100 °C
Reagent 2 = OPA Reagent
Fluorescence Detector: Excitation = 340 ηm
Emission = 450 ηm
Time constant = 2.0 sec

Retention Time:		
	Aldicarb SO	-10.2
	Aldicarb SO2	-11.3
	Oxamyl	-1 1.4
	Methomyl	-11.9
	Mesurol SO	-12.9
	3 OH-Carbofuran	-13.5
	Mesurol SO2	-14.8
	Aldicarb	-15.7
	Carbofuran	-17.3
	Carbaryl	-17.8
	Mesurol	-20.0

Calculations:

$$ppb = \frac{\text{(sample peak ht.)(response factor, ηg)(sample final vol., mL)(1000µL/mL)}}{\text{(sample vol. injected, µL)(sample wt., g)}}$$

$$\text{where: response factor (ηg)} = \frac{\Sigma[\text{ (std. conc.}_n\text{, ηg/µL) (std. vol. injected, µL)/ (std. peak ht.,)}]}{n}$$

n = number of standards

Method Performance:

Quality Control.

1. A 4-point calibration curve of 0.025, 0.05, 0.1, and 0.4ηg/µL was obtained at the beginning and the end of each set of samples for the response factor calculating.
2. Each sample shall be injected two times to insure reliability of the analysis. If the signal of a sample is greater than that of the highest standard in the calibration curve, dilute the sample. Re-inject the diluted sample together with standards twice more. A sample set is comprised of 10 samples, a blank and a spike.

Method Detection Limit (MDL).

Method Detection Limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably in either a sample or a blank. To determine the MDL, 7 samples each containing 100 ± 1 g of background water were spiked with 0.1 ppb and process each through the entire method along with a blank. The standard deviation was computed from the 7 results (ppb). The MDL was computed as follows:

$$MDL = St$$

where:

t is the student's "t" value for the 99% confidence level with n-l degrees of freedom (n-l, $1 - \alpha = 0.99$). n represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses.

The results for the standard deviations and MDL are in Appendix 1.

Reporting Limit (RL):

Reporting Limit (RL) refers to level above which quantitative results may be obtained. In this method the RL is set at 2 times the MDL or 0.05 ppb.

Recovery Data:

Method validation was made by preparing five sets of spike samples. Each set contained a blank and five levels of spikes. The background water (American River water) was obtained from Department of Pesticide Regulation. Each set was processed through the entire analytical method on separate days. Recovery for the carbamates is shown in Appendix 2.

Discussion:

It is our experience that some of the carbamates are heat sensitive. To achieve acceptable recoveries, prolonged heating must be avoided and the recommended temperature must be followed during evaporation to prevent low recoveries. We also found that it may be necessary to silazine the round bottom flask to prevent absortion into scratched or etched glass. See SOP Preparation and Use of a Silazining Reagent.

References:

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4. Keith, Lawrence H., etc., *Principals of Environmental Analysis, Anal. Chem.,* 1983, 55, 22 1 O-22 18

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Appendix 1:

MDL Determination

	Aldicarb SO		Oxamyl		Mesurol SO		Aldicarb	
	ppb	%	ppb	%	ppb	%	ppb	%
spk 1	0.0606	60.6	0.0974	97.4	0.0978	97.7	0.0794	79.4
spk 2	0.0658	65.8	0.094 1	94.1	0.0986	98.6	0.0796	79.6
spk 3	0.0634	63.4	0.103	103	0.0839	83.9	0.0839	83.9
spk 4	0.0672	67.2	0.0898	89.8	0.0830	83	0.0799	79.8
spk 5	0.0765	76.5	0.0987	98.7	0.0989	98.9	0.0885	88.5
spk 6	0.0698	69.8	0.0844	84.4	0.0867	86.7	0.0850	85.0
spk 7	0.048 1	48.1	0.0805	80.5	0.0793	79.3	0.0689	68.9
STDEV	0.0088		0.0081		0.0084		0.0062	
MDL	0.0277		0.0255		0.0264		0.0196	
RL	0.05		0.05		0.05		0.05	

	Carbaryl		Aldicarb-SO2		Methomyl		3OH-Carbofuran	
	ppb	%	ppb	%	ppb	%	ppb	%
spk 1	0.0953	95.3	0.0857	85.7	0.0779	77.9	0.0850	85
spk 2	0.0942	94.2	0.0911	91.1	0.0912	91.2	0.100	100
spk 3	0.0994	99.4	0.0760	76	0.0778	77.8	0.0865	86.5
spk 4	0.0907	90.7	0.0942	94.2	0.0897	89.7	0.0923	92.3
spk 5	0.0944	94.4	0.0847	84.7	0.0708	70.8	0.0863	86.3
spk 6	0.0886	88.6	0.0882	88.2	0.0809	80.9	0.0879	87.9
spk 7	0.0866	86.8	0.0769	76.9	0.0692	69.2	0.0758	75.8
STDEV	0.0043		0.0068		0.0085		0.0074	
MDL	0.0136		0.0214		0.0265		0.0232	
RL	0.05		0.05		0.05		0.05	

	Mesurol-SO2		Carbofuran		Mesurol	
	ppb	%	ppb	%	ppb	%
spk 1	0.0876	87.6	0.0829	82.9	0.0852	85.1
spk 2	0.0903	90.3	0..091	91	0.0905	90.5
spk 3	0.0772	77.1	0.0723	72.3	0.0884	88.4
spk 4	0.096 1	96.1	0.0924	92.4	0.0972	97.2
spk 5	0.0915	91.5	0.0846	84.6	0.085 1	85.1
spk 6	0.0873	87.3	0.0832	83.2	0.0775	77.5
spk 7	0.0684	68.4	0.0734	73.4	0.07 11	71.1
STDEV	0.0095		0.0078		0.0086	
MDL	0.0299		0.0244		0.0270	
RL	0.05		0.05		0.05	

Appendix: 2

Validation Results

	Aldicarb SO		Oxamyl		Mesurol SO		Aldicarb	
levels	ppb	%	ppb	%	ppb	%	ppb	%
0.1	0.0638	63.8	0.0940	94.0	0.0884	88.4	0.0919	91.9
0.1	0.0660	66.0	0.100	100	0.103	103	0.0928	92.8
0.1	0.0726	72.6	0.102	102	0.0858	85.8	0.0770	77.0
0.1	0.0724	72.4	0.0953	95.3	0.0966	96.6	0.0764	76.4
0.1	0.057 1	57.1	0.0853	85.3	0.0871	87.1	0.0734	73.4
0.2	0.126	63.0	0.181	90.5	0.182	91.0	0.155	77.5
0.2	0.130	65.0	0.190	95.0	0.194	97.0	0.144	72.0
0.2	0.132	66.0	0.181	90.5	0.167	83.5	0.130	65.0
0.2	0.135	67.5	0.184	92.0	0.169	84.5	0.147	73.5
0.2	0.128	64.0	0.187	93.5	0.176	88.0	0.157	78.5
0.5	0.341	68.2	0.474	94.8	0.453	90.6	0.424	84.8
0.5	0.363	72.6	0.511	102	0.526	105	0.440	88.0
0.5	0.363	72.6	0.504	101	0.453	90.6	0.376	75.2
0.5	0.305	61.0	0.422	84.4	0.406	81.2	0.395	79.0
0.5	0.336	67.2	0.490	98.0	0.43 1	86.2	0.350	70.0
1	0.626	62.6	0.930	93.0	0.882	88.2	0.766	76.6
1	0.670	67.0	0.956	95.6	0.971	97.1	0.842	84.2
1	0.642	64.2	0.929	92.9	0.841	84.1	0.745	74.5
1	0.683	68.3	0.944	94.4	0.910	91.0	0.681	68.1
1	0.601	60.1	0.868	86.8	0.837	83.7	0.618	61.8
4	2.74	68.5	3.95	98.8	3.78	94.5	3.74	93.5
4	2.73	68.3	3.77	94.3	3.80	95.0	3.46	86.5
4	2.48	62.0	3.82	95.5	3.45	86.3	3.44	86.0
4	2.76	69.0	3.95	98.8	3.68	92.0	3.38	84.5
4	2 . 7 5	68.8	4.21	105	4.06	102	4.04	. 101

Appendix *2:continued*

Validation Results

	Carbaryl		Aldicarb-SO2		Methomyl		3OH-Carbofuran	
levels	ppb	%	ppb	%	ppb	%	ppb	%
0.1	0.0939	93.9	0.0962	96.2	0.0963	96.3	0.109	109
0.1	0.0990	99.0	0.0793	79.3	0.0692	69.2	0.0876	87.6
0.1	0.0926	92.6	0.0850	85.0	0.0728	72.8	0.100	100
0.1	0.0987	98.7	0.0964	96.4	0.0986	98.6	0.103	103
0.1	0.0919	91.9	0.0924	92.4	0.0929	92.9	0.107	107
0.2	0.175	87.5	0.158	79.0	0.154	77.0	0.186	93.0
0.2	0.188	94.0	0.183	91.5	0.177	88.5	0.175	87.5
0.2	0.173	86.5	0.199	99.5	0.181	90.5	0.201	101
0.2	0.181	90.5	0.191	95.5	0. 192	96.0	0.207	104
0.2	0.181	90.5	0.185	92.5	0.173	86.5	0.203	102
0.5	0.439	87.8	0.459	91.8	0.416	83.2	0.499	99.8
0.5	0.48 1	96.2	0.480	96.0	0.458	91.6	0.470	94.0
0.5	0.486	97.2	0.436	87.2	0.45 1	90.2	0.487	97.4
0.5	0.438	87.6	0.474	94.8	0.43 1	86.2	0.456	91.2
0.5	0.460	92.0	0.420	84.0	0.406	81.2	0.465	93.0
1	0.862	86.2	0.947	94.7	0.923	92.3	0.964	96.4
1	0.934	93.4	0.984	98.4	0.843	84.3	0.956	95.6
1	0.927	92.7	0.952	95.2	0.922	92.2	0.910	91.0
1	0.934	93.4	1.05	105	0.914	91.4	1.06	106
1	0.890	89.0	0.920	92.0	0.761	76.1	0.904	90.4
4	3.86	96.5	3.57	89.3	3.58	89.5	3.72	93.0
4	3.74	93.5	3.77	94.3	3.64	91.0	3.71	92.8
4	3.82	95.5	3.72	93.0	3.75	93.8	3.72	93.0
4	3.97	99.3	3.89	97.3	3.92	98.0	3.98	99.5
4	4.09	102	3.96	99.0	3.94	98.5	3.83	95.8

Appendix 2:*continued*

Validation Results

	Mesurol-SO2		**Carbofuran**		**Mesurol**	
levels	ppb	%	ppb	%	ppb	%
0.1	0.116	116	0.0960	96.0	0.112	112
0.1	0.0872	87.2	0.0724	72.4	0.0840	84.0
0.1	0.0758	75.8	0.0689	68.9	0.0803	80.3
0.1	0.101	101	0.0930	93.0	0.0960	96.0
0.1	0.0968	96.8	0.0933	93.3	0.0973	97.3
0.2	0.174	87.0	0. 161	80.5	0.165	82.5
0.2	0.185	92.5	0.183	91.5	0.185	92.5
0.2	0.209	105	0.186	93.0	0.200	100
0.2	0.206	103	0.198	99.0	0.195	97.5
0.2	0.168	84.0	0.178	89.0	0.178	89.0
0.5	0.495	99.0	0.435	87.0	0.479	95.8
0.5	0.495	99.0	0.438	87.6	0.472	94.4
0.5	0.463	92.6	0.420	84.0	0.395	79.0
0.5	0.570	114	0.42 1	84.2	0.469	93.8
0.5	0.493	98.6	0.544	109	0.435	87.0
1	1.04	104	0.993	99.3	0.988	98.8
1	0979	97.9	0.880	88.0	0.960	96.0
1	1.02	102	0.912	91.2	0.840	84.0
1	1.11	111	0.97 1	97.1	1 .00	100
1	0.870	87.0	0.804	80.4	0.866	86.6
4	3.70	92.5	3.70	92.5	3.65	91.3
4	3.85	96.3	3.70	92.5	3.69	92.3
4	4.15	104	3.78	94.5	3.74	93.5
4	4.55	114	3.94	98.5	4.13	103
4	4.18	105	3.93	98.3	3.96	99.0

APPENDIX IV
Continuing Quality Control

Appendix IV. Continuing Quality Control- Glyphosate Screen

Table 1. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen:Glyphosate	UCL= 94.2	Sample type: Surface Water
Analyte: Glyphosate	UWL= 86.9	Lab: CDFA
RL: 2.00 ppb	LWL= 57.5	Chemist: Hsaio Feng
	LCL= 50.2	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-3, 11, 19, 27	8.0	6.230	77.9			
171-303, 308, 312, 332, 351	8.0	7.260	90.8			
170-34, 51, 59, 75						
171-340, 344, 348, 359	8.0	8.090	101.1**			
170-39, 47, 63, 71, 201						
171-367, 371, 375, 382, 449	4.0	2.900	72.5	3.16	79.0	8.58
170-87, 95, 206, 218, 229						
171-387, 391, 395, 418, 453	4.0	3.040	76.0	3.55	88.8	15.48

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

** Matrix spike recovery fell above the upper control limit.

Appendix IV. Continuing Quality Control- Organophosphate Screen

Table 1. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 109.8	Sample type: Surface Water
Analyte: DDVP	UWL= 102.3	Lab: CDFA
RL: 0.05 ppb	LWL= 72.2	Chemist: Jorge L. Hernandez
	LCL= 64.7	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.085	85.0			
171-325, 333	0.1	0.075	75.0			
170-29, 52, 76						
171-352, 360	0.1	0.085	85.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.104	104.0			
170-88, 96, 219						
171-396, 419	0.1	0.073	73.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 2. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 119.5	Sample type: Surface Water
Analyte: Dimethoate	UWL= 112.7	Lab: CDFA
RL: 0.05 ppb	LWL= 85.6	Chemist: Jorge L. Hernandez
	LCL= 78.8	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.109	109.0			
171-325, 333	0.1	0.095	95.0			
170-29, 52, 76						
171-352, 360	0.1	0.094	94.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.107	107.0			
170-88, 96, 219						
171-396, 419	0.1	0.090	90.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 3. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 108.7	Sample type: Surface Water
Analyte: Diazinon	UWL= 102.5	Lab: CDFA
RL: 0.04 ppb	LWL= 77.6	Chemist: Jorge L. Hernandez
	LCL= 71.4	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.08	0.079	98.8			
171-325, 333	0.08	0.073	91.3			
170-29, 52, 76						
171-352, 360	0.08	0.074	92.5			
170-40, 64, 72, 200						
171-376, 384, 448	0.08	0.068	85.0			
170-88, 96, 219						
171-396, 419	0.08	0.070	87.5			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 4. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 117.7	Sample type: Surface Water
Analyte: M. Parathion	UWL= 110.7	Lab: CDFA
RL: 0.05 ppb	LWL= 82.7	Chemist: Jorge L. Hernandez
	LCL= 75.7	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.107	107.0			
171-325, 333	0.1	0.093	93.0			
170-29, 52, 76						
171-352, 360	0.1	0.081	81.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.091	91.0			
170-88, 96, 219						
171-396, 419	0.1	0.091	91.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 5. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 113.1	Sample type: Surface Water
Analyte: Malathion	UWL= 106.9	Lab: CDFA
RL: 0.05 ppb	LWL= 82.3	Chemist: Jorge L. Hernandez
	LCL= 76.1	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.107	107.0			
171-325, 333	0.1	0.096	96.0			
170-29, 52, 76						
171-352, 360	0.1	0.088	88.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.096	96.0			
170-88, 96, 219						
171-396, 419	0.1	0.089	89.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 6. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 112.2	Sample type: Surface Water
Analyte: Chlorpyrifos	UWL= 106.1	Lab: CDFA
RL: 0.04 ppb	LWL= 81.8	Chemist: Jorge L. Hernandez
	LCL= 75.7	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.08	0.083	103.8			
171-325, 333	0.08	0.075	93.8			
170-29, 52, 76						
171-352, 360	0.08	0.065	81.3			
170-40, 64, 72, 200						
171-376, 384, 448	0.08	0.068	85.0			
170-88, 96, 219						
171-396, 419	0.08	0.069	86.3			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 7. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 119.7	Sample type: Surface Water
Analyte: Methidathion	UWL= 112.5	Lab: CDFA
RL: 0.05 ppb	LWL= 83.8	Chemist: Jorge L. Hernandez
	LCL= 76.6	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.108	108.0			
171-325, 333	0.1	0.094	94.0			
170-29, 52, 76						
171-352, 360	0.1	0.109	109.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.096	96.0			
170-88, 96, 219						
171-396, 419	0.1	0.093	93.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 8. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 120.0	Sample type: Surface Water
Analyte: Phosmet	UWL= 112.9	Lab: CDFA
RL: 0.05 ppb	LWL= 84.5	Chemist: Jorge L. Hernandez
	LCL= 77.4	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.116	116.0			
171-325, 333	0.1	0.105	105.0			
170-29, 52, 76						
171-352, 360	0.1	0.111	111.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.105	105.0			
170-88, 96, 219						
171-396, 419	0.1	0.094	94.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 9. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 121.5	Sample type: Surface Water
Analyte: Azinphos-methyl	UWL= 114.7	Lab: CDFA
RL: 0.05 ppb	LWL= 87.4	Chemist: Jorge L. Hernandez
	LCL= 80.6	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.119	119.0			
171-325, 333	0.1	0.103	103.0			
170-29, 52, 76						
171-352, 360	0.1	0.107	107.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.108	108.0			
170-88, 96, 219						
171-396, 419	0.1	0.100	100.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 10. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 110.9	Sample type: Surface Water
Analyte: Ethoprop	UWL= 104.2	Lab: CDFA
RL: 0.05 ppb	LWL= 77.6	Chemist: Jorge L. Hernandez
	LCL= 70.9	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.087	87.0			
171-325, 333	0.1	0.093	93.0			
170-29, 52, 76						
171-352, 360	0.1	0.078	78.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.079	79.0			
170-88, 96, 219						
171-396, 419	0.1	0.089	89.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 11. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 107.3	Sample type: Surface Water
Analyte: Phorate	UWL= 99.9	Lab: CDFA
RL: 0.05 ppb	LWL= 70.4	Chemist: Jorge L. Hernandez
	LCL= 63.1	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.071	71.0			
171-325, 333	0.1	0.093	93.0			
170-29, 52, 76						
171-352, 360	0.1	0.076	76.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.078	78.0			
170-88, 96, 219						
171-396, 419	0.1	0.087	87.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 12. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 110.6	Sample type: Surface Water
Analyte: Fonofos	UWL= 103.2	Lab: CDFA
RL: 0.05 ppb	LWL= 73.6	Chemist: Jorge L. Hernandez
	LCL= 66.3	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.085	85.0			
171-325, 333	0.1	0.091	91.0			
170-29, 52, 76						
171-352, 360	0.1	0.080	80.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.084	84.0			
170-88, 96, 219						
171-396, 419	0.1	0.088	88.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 13. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 120.4	Sample type: Surface Water
Analyte: E. Parathion	UWL= 112.0	Lab: CDFA
RL: 0.05 ppb	LWL= 78.3	Chemist: Jorge L. Hernandez
	LCL= 69.8	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.100	100.0			
171-325, 333	0.1	0.093	93.0			
170-29, 52, 76						
171-352, 360	0.1	0.089	89.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.081	81.0			
170-88, 96, 219						
171-396, 419	0.1	0.095	95.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 14. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Organophosphate	UCL= 118.9	Sample type: Surface Water
Analyte: Phosalone	UWL= 112.0	Lab: CDFA
RL: 0.05 ppb	LWL= 84.7	Chemist: Jorge L. Hernandez
	LCL= 77.8	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170- 4, 12, 20	0.1	0.102	102.0			
171-325, 333	0.1	0.110	110.0			
170-29, 52, 76						
171-352, 360	0.1	0.099	99.0			
170-40, 64, 72, 200						
171-376, 384, 448	0.1	0.100	100.0			
170-88, 96, 219						
171-396, 419	0.1	0.096	96.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Appendix IV. Continuing Quality Control- Carbamate Screen

Table 1. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Carbamate	UCL= 108.2	Sample type: Surface Water
Analyte: Aldicarb	UWL= 98.7	Lab: CDFA
RL: 0.05 ppb	LWL= 60.6	Chemist: Hsaio Feng
	LCL= 51.1	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-5, 13, 21	0.1	0.0753	75.3			
171-326, 334	0.1	0.0830	83.0			
170-30, 53, 77						
171-353, 361	0.1	0.0833	83.3			
170-41, 65, 81						
171-377, 400	0.1	0.0753	75.3	0.0878	87.8	15.33
170-89, 220, 224						
171-412, 421	0.1	0.0820	82.0	0.0712	71.2	14.10

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 2. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Carbamate	UCL= 106.0	Sample type: Surface Water
Analyte: Carbaryl	UWL= 101.7	Lab: CDFA
RL: 0.05 ppb	LWL= 84.5	Chemist: Hsaio Feng
	LCL= 80.2	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-5, 13, 21	0.1	0.0940	94.0			
171-326, 334	0.1	0.0886	88.6			
170-30, 53, 77						
171-353, 361	0.1	0.0901	90.1			
170-41, 65, 81						
171-377, 400	0.1	0.0922	92.2	0.1110	111.0**	18.50
170-89, 220, 224						
171-412, 421	0.1	0.0937	93.7	0.0850	85.0	9.74

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

** Matrix spike recovery fell above the upper control limit.

Table 3. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Carbamate	UCL= 116.7	Sample type: Surface Water
Analyte: Carbofuran	UWL= 108.0	Lab: CDFA
RL: 0.05 ppb	LWL= 72.9	Chemist: Hsaio Feng
	LCL= 64.1	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-5, 13, 21	0.1	0.0913	91.3			
171-326, 334	0.1	0.0861	86.1			
170-30, 53, 77						
171-353, 361	0.1	0.0914	91.4			
170-41, 65, 81						
171-377, 400	0.1	0.0869	86.9	0.0912	91.2	4.83
170-89, 220, 224						
171-412, 421	0.1	0.0899	89.9	0.0803	80.3	11.28

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 4. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Carbamate	UCL= 116.1	Sample type: Surface Water
Analyte: Mesurol	UWL= 108.4	Lab: CDFA
RL: 0.05 ppb	LWL= 77.6	Chemist: Hsaio Feng
	LCL= 69.9	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-5, 13, 21	0.1	0.0941	94.1			
171-326, 334	0.1	0.0946	94.6			
170-30, 53, 77						
171-353, 361	0.1	0.0807	80.7			
170-41, 65, 81						
171-377, 400	0.1	0.0897	89.7	0.0957	95.7	6.47
170-89, 220, 224						
171-412, 421	0.1	0.0959	95.9	0.0847	84.7	12.40

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 5. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Carbamate	UCL= 112.3	Sample type: Surface Water
Analyte: Methomyl	UWL= 104.3	Lab: CDFA
RL: 0.05 ppb	LWL= 72.3	Chemist: Hsaio Feng
	LCL= 64.4	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-5, 13, 21	0.1	0.0891	89.1			
171-326, 334	0.1	0.0865	86.5			
170-30, 53, 77						
171-353, 361	0.1	0.0937	93.7			
170-41, 65, 81						
171-377, 400	0.1	0.0857	85.7	0.0887	88.7	3.44
170-89, 220, 224						
171-412, 421	0.1	0.0891	89.1	0.0789	78.9	12.14

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 6. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Carbamate	UCL= 110.3	Sample type: Surface Water
Analyte: Oxamyl	UWL= 105.2	Lab: CDFA
RL: 0.05 ppb	LWL= 84.7	Chemist: Hsaio Feng
	LCL= 79.5	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-5, 13, 21	0.1	0.0977	97.7			
171-326, 334	0.1	0.0941	94.1			
170-30, 53, 77						
171-353, 361	0.1	0.0931	93.1			
170-41, 65, 81						
171-377, 400	0.1	0.0903	90.3	0.0989	98.9	9.09
170-89, 220, 224						
171-412, 421	0.1	0.0975	97.5	0.0898	89.8	8.22

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Appendix IV. Continuing Quality Control- Phenoxy Screen

Table 1. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Phenoxy	UCL= 126.5	Sample type: Surface Water
Analyte: MCPA	UWL= 116.3	Lab: CDFA
RL: 0.10 ppb	LWL= 75.4	Chemist: Jean Hsu
	LCL= 65.1	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-2, 10, 18, 26	0.2	0.154	77.0			
171-302, 307, 331, 350	0.2	0.169	84.5			
170-33, 50, 74						
171-339, 343, 347, 358	0.2	0.177	88.5			
170-38, 46, 62, 70, 202						
171-366, 370, 374, 382, 450	0.2	0.192	96.0	0.211	105.5	9.43
170-86, 94, 205, 217, 234	0.2	0.214	107.0	0.192	96.0	10.84
171-386, 390, 394, 417, 458	0.2	0.198	99.0	0.209	104.5	5.41

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 2. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Phenoxy	UCL= 128.5	Sample type: Surface Water
Analyte: 2,4-D	UWL= 116.3	Lab: CDFA
RL: 0.10 ppb	LWL= 67.6	Chemist: Jean Hsu
	LCL= 55.5	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-2, 10, 18, 26	0.2	0.156	78.0			
171-302, 307, 331, 350	0.2	0.187	93.5			
170-33, 50, 74						
171-339, 343, 347, 358	0.2	0.191	95.5			
170-38, 46, 62, 70, 202						
171-366, 370, 374, 382, 450	0.2	0.152	76.0	0.183	91.5	18.51
170-86, 94, 205, 217, 234	0.2	0.225	112.5	0.219	109.5	2.70
171-386, 390, 394, 417, 458	0.2	0.194	97.0	0.219	109.5	12.11

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Table 3. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Phenoxy	UCL= 146.9	Sample type: Surface Water
Analyte: Triclopyr	UWL= 134.1	Lab: CDFA
RL: 0.10 ppb	LWL= 83.2	Chemist: Jean Hsu
	LCL= 70.4	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-2, 10, 18, 26	0.2	0.153	76.5			
171-302, 307, 331, 350	0.2	0.186	93.0			
170-33, 50, 74						
171-339, 343, 347, 358	0.2	0.216	108.0			
170-38, 46, 62, 70, 202						
171-366, 370, 374, 382, 450	0.2	0.190	95.0	0.208	104.0	9.05
170-86, 94, 205, 217, 234	0.2	0.245	122.5	0.208	104.0	16.34
171-386, 390, 394, 417, 458	0.2	0.204	102.0	0.219	109.5	7.09

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Appendix IV. Continuing Quality Control- Diazinon Screen

Table 1. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Diazinon	UCL= 108.7	Sample type: Surface Water
Analyte: Diazinon	UWL= 102.5	Lab: CDFA
RL: 0.04 ppb	LWL= 77.6	Chemist: Jorge L. Hernandez
	LCL= 71.4	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-6, 14, 22	0.08	0.075	93.8			
171-327, 335	0.08	0.072	90.0			
170-31, 54, 78						
171-354, 362	0.08	0.074	92.5			
170-42, 66, 82						
171-378, 401	0.08	0.081	101.3	0.078	97.5	3.77
170-90, 221, 225, 235						
171-413, 420, 459	0.08	0.080	100.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

Appendix IV. Continuing Quality Control- Triazine Screen

Table 1. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 122.8	Sample type: Surface Water
Analyte: Hexazinone	UWL= 115.1	Lab: CDFA
RL: 0.20 ppb	LWL= 84.5	Chemist: Duc Tran
	LCL= 76.8	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.405	80.9			
171-301, 306, 310, 330, 349						
170-32, 49, 57, 73	0.5	0.422	84.4			
171-338, 342, 346, 357						
170-37, 45, 61, 69, 203	0.5	0.498	99.6			
171-365, 369, 373, 381, 451						
170-37, 45, 61, 69, 203	0.4	0.338	84.5			
171-365, 369, 373, 381, 451[1]						
170-85, 93, 204, 216, 228	6.0	6.160	102.7			
171-385, 389, 393, 416, 452	0.4	0.414	103.5			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

Table 2. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 120.6	Sample type: Surface Water
Analyte: Cyanazine	UWL= 114.0	Lab: CDFA
RL: 0.20 ppb	LWL= 87.4	Chemist: Duc Tran
	LCL= 80.7	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.404	80.8			
171-301, 306, 310, 330, 349						
170-32, 49, 57, 73	0.5	0.554	110.8			
171-338, 342, 346, 357						
170-37, 45, 61, 69, 203	0.5	0.420	84.0			
171-365, 369, 373, 381, 451						
170-37, 45, 61, 69, 203	0.4	0.399	99.8			
171-365, 369, 373, 381, 451[1]						
170-85, 93, 204, 216, 228	6.0	6.720	112.0			
171-385, 389, 393, 416, 452	0.4	0.420	105.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

Table 3. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 105.0	Sample type: Surface Water
Analyte: Metribuzin	UWL= 100.9	Lab: CDFA
RL: 0.20 ppb	LWL= 84.5	Chemist: Duc Tran
	LCL= 80.4	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.398	79.6*			
171-301, 306, 310, 330, 349	0.5	0.464	92.8			
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.480	96.0			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.4	0.345	86.3			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	6.830	113.8**			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.4	0.428	107.0**			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

* Matrix spike recovery fell below the lower control limit.

** Matrix spike recovery fell above the upper control limit

Table 4. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 121.4	Sample type: Surface Water
Analyte: Atrazine	UWL= 114.1	Lab: CDFA
RL: 0.05 ppb	LWL= 85.0	Chemist: Duc Tran
	LCL= 77.7	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.400	80.0			
171-301, 306, 310, 330, 349	0.5	0.446	89.2			
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.496	99.2			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.1	0.114	114.0			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	5.490	91.5			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.1	0.088	88.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

Table 5. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 125.7	Sample type: Surface Water
Analyte: Simazine	UWL= 117.8	Lab: CDFA
RL: 0.05 ppb	LWL= 86.4	Chemist: Duc Tran
	LCL= 78.5	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.448	89.6			
171-301, 306, 310, 330, 349						
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.432	86.4			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.1	0.091	91.0			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	6.780	113.0			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.1	0.110	110.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

Table 6. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 116.7	Sample type: Surface Water
Analyte: Diuron	UWL= 108.3	Lab: CDFA
RL: 0.05 ppb	LWL= 74.6	Chemist: Duc Tran
	LCL= 66.2	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.432	86.4			
171-301, 306, 310, 330, 349						
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.534	106.8			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.1	0.118	118.0**			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	5.590	93.2			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.1	0.112	112.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

**Matrix spike recovery fell above the upper control limit

Table 7. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 110.6	Sample type: Surface Water
Analyte: Prometon	UWL= 103.6	Lab: CDFA
RL: 0.05 ppb	LWL= 75.9	Chemist: Duc Tran
	LCL= 68.9	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.431	86.2			
171-301, 306, 310, 330, 349	0.5	0.512	102.4			
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.476	95.2			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.1	0.093	93.0			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	6.760	112.7**			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.1	0.099	99.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

**Matrix spike recovery fell above the upper control limit

Table 8. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 114.5	Sample type: Surface Water
Analyte: Bromacil	UWL= 108.9	Lab: CDFA
RL: 0.05 ppb	LWL= 86.5	Chemist: Duc Tran
	LCL= 80.9	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.469	93.8			
171-301, 306, 310, 330, 349	0.5	0.442	88.4			
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.498	99.6			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.1	0.095	95.0			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	6.180	103.0			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.1	0.091	91.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

Table 9. Continuing QC for the Klamath River Watershed- Study 170 and 171

Screen: Triazine	UCL= 115.3	Sample type: Surface Water
Analyte: Prometryn	UWL= 108.1	Lab: CDFA
RL: 0.05 ppb	LWL= 79.1	Chemist: Duc Tran
	LCL= 71.9	

Sample Analyzed with Each Extraction Set (Sample Number)	Spike Level (ppb)	Results (ppb)	Recovery (%)	Duplicate Spike Results	Recovery (%)	% Difference
170-1, 9, 17, 25	0.5	0.465	93.0			
171-301, 306, 310, 330, 349	0.5	0.524	104.8			
170-32, 49, 57, 73						
171-338, 342, 346, 357	0.5	0.494	98.8			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451	0.1	0.094	94.0			
170-37, 45, 61, 69, 203						
171-365, 369, 373, 381, 451[1]	6.0	6.370	106.2			
170-85, 93, 204, 216, 228						
171-385, 389, 393, 416, 452	0.1	0.096	96.0			

UCL= upper control limit, UWL= upper warning limit, LWL= lower warning limit, LCL= lower control limit

1- deviation: double spikes instead of duplicate spikes.

APPENDIX V
Blind Spike Results

Appendix V. Blind Spike Results

Blind Spike Data for the Klamath River Watershed- Study 170 and 171 (1998-1999)				
Analyte	Spike Level (ppb)	Results (ppb)	Recovery (%)	Date Analyzed
Triazine Screen				
Atrazine	0.2	0.177	88.5	10/5/98
	0.1	0.090	90.0	6/28/99
	0.1	0.100	100.0	6/28/99
Hexazinone	0.2	0.167*	83.5	10/5/98
	0.4	0.420	105.0	6/28/99
	0.4	0.420	105.0	6/28/99
	0.4	0.430	107.5	11/9/99
	0.4	0.390	97.5	11/9/99
Simazine	0.2	0.188	94.0	11/9/99
	0.2	0.193	96.5	11/9/99
Phenoxy Screen				
2,4-D	0.2	0.166	83.0	10/7/98
	0.2	0.145	72.5	6/25/99
	0.2	0.160	80.0	6/25/99
	0.2	0.200	100.0	11/2/99
	0.2	0.170	85.0	11/5/99
Triclopyr	0.3	0.242	80.7	10/7/98
	0.3	0.281	93.7	6/25/99
	0.3	0.264	88.0	6/25/99
	0.2	0.186	93.0	11/2/99
	0.2	0.172	86.0	11/5/99
Glyphosate Screen	5.0	3.820	76.4	10/20/98
	2.0	1.91*	95.5**	7/1/99
	2.0	1.81*	90.5	7/1/99
	4.0	4.020	100.5**	11/9/99
	4.0	3.510	87.8	11/9/99
Organophosphate Screen				
Chlorpyrifos	0.1	0.081	81.0	6/29/99
	0.1	0.085	85.0	6/29/99

Blind Spike Data for the Klamath River Watershed- Study 170 and 171 (1998-1999)

Analyte	Spike Level (ppb)	Results (ppb)	Recovery (%)	Date Analyzed
Dimethoate	0.1	0.106	106.0	6/29/99
	0.1	0.105	105.0	6/29/99
Diazinon Screen	0.2	0.162	81.0	11/1/99
	0.2	0.178	89.0	11/1/99

* Spikes requested at the reporting limits. Therefore, recoveries were reported as ND, although trace amounts were recovered.

** Matrix spike recovery fell above the upper control limit.

Appendix VI. Field Rinse Sample Results

Field Rinse Sample for the Klamath River Watershed- Study 170 and 171 (1998-1999)							
Date	Site[a]	TR[b]	PH[c]	GL[d]	OP[e]	CB[f]	DI[g]
9/23/98	Scott River	ND[h]	ND	ND	ND	ND	ND
9/30/98	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND
10/25/98	Scott River	ND	ND	ND	ND	ND	ND
10/25/98	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND
6/22/99	Klamath R. @ Horse Cr.	ND	ND	ND	ND	ND	ND
6/22/00	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND
10/28/99	Klamath R. @ Horse Cr.	ND	ND	ND	ND	ND	ND
10/28/99	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND

a. Site descriptions are listed in Table 1.
b. Triazines (see Appendix IV for a list of herbicides and reporting limits).
c. Phenoxys (see Appendix IV for a list of herbicides and reporting limits).
d. Glyphosate (see Appendix IV for a list of herbicides and reporting limits).
e. Organophosphates (see Appendix IV for a list of insecticides and reporting limits).
f. Carbamates (see Appendix IV for a list of insecticides and reporting limits).
g. Diazinon (see Appendix IV for a list of insecticides and reporting limits).
h. None detected.

APPENDIX VI
Field Rinse Sample Results

Appendix VI. Field Rinse Sample Results

Field Rinse Sample for the Klamath River Watershed- Study 170 and 171 (1998-1999)							
Date	Site[a]	TR[b]	PH[c]	GL[d]	OP[e]	CB[f]	DI[g]
9/23/98	Scott River	ND[h]	ND	ND	ND	ND	ND
9/30/98	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND
10/25/98	Scott River	ND	ND	ND	ND	ND	ND
10/25/98	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND
6/22/99	Klamath R. @ Horse Cr.	ND	ND	ND	ND	ND	ND
6/22/00	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND
10/28/99	Klamath R. @ Horse Cr.	ND	ND	ND	ND	ND	ND
10/28/99	Trinity R. @ Tish Tang	ND	ND	ND	ND	ND	ND

a. Site descriptions are listed in Table 1.
b. Triazines (see Appendix IV for a list of herbicides and reporting limits).
c. Phenoxys (see Appendix IV for a list of herbicides and reporting limits).
d. Glyphosate (see Appendix IV for a list of herbicides and reporting limits).
e. Organophosphates (see Appendix IV for a list of insecticides and reporting limits).
f. Carbamates (see Appendix IV for a list of insecticides and reporting limits).
g. Diazinon (see Appendix IV for a list of insecticides and reporting limits).
h. None detected.